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## ANALYTICAL ABSTRACTS

## 1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

1. Error control in routine analysis. K. Doerffel (Inst. für anal. Chemie, Tech. Hochschule für Chemie, Leuna-Merseburg). *Chem. Tech., Berlin*, 1958, 10 (3), 151-152.—A simple statistical procedure is described for establishing the accuracy of an analytical method. The method consists in obtaining the systematic error  $\epsilon$  and proportional error  $\alpha$  for each sample of a series (duplicate determinations) and finding the mean  $\bar{\epsilon}$  and  $\bar{\alpha}$ , which for error-free determinations should be  $\bar{\epsilon} = 0$  and  $\bar{\alpha} = 1.0$ . From these values one obtains the  $t$  values, thus  $t_{\epsilon} = \bar{\epsilon}/s_{\epsilon}n^{-0.5}$  and  $t_{\alpha} = \text{mod. } (1 - \bar{\alpha})/s_{\alpha}n^{-0.5}$  where  $s$  is the standard variation of  $\epsilon$  and  $\alpha$  values about the mean  $\bar{\epsilon}$  and  $\bar{\alpha}$  and  $n$  is the number of the  $\epsilon$  and  $\alpha$  values used. These  $t$  values are compared with the standard tabular  $t$  values for known  $n$ ; a satisfactory value is that for statistical accuracy of 95%.

J. L. PROSSER

2. *o*-Dithiols in analysis. VII. Toluene-3:4-dithiol as a general reagent in qualitative analysis. R. E. D. Clark (Dept. of Sci. and Technol., Cambs. Tech. Coll. and School of Art, Cambridge, England). *Analyst*, 1958, 83, 396-402.—The properties of toluene-3:4-dithiol (dithiol) resemble those of  $H_2S$  and it can serve as a convenient substitute for  $H_2S$  in analysis. Its metal complexes formed in acid soln. show marked colour contrasts. The conditions of pptn. are given for 34 cations.

A. O. JONES

3. Analytical use of the organic reagent *o*-(2-amino-1-naphthylazo)benzoic acid. N. M. Vital'skaya. *Uch. Zap. Yaroslavsk. Tekhnol. Inst.*, 1957, 2, 65-72; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,007.—Description is given of the properties and possible use of *o*-(2-amino-1-naphthylazo)benzoic acid (I) or its sodium salt for the detection of various metals including Cu, Co, Zn, Pd, Mn, Fe, Pb, Ca, Mg, Al, Cr, Ag, Hg, Bi and Sn. The quantitative determination of Zn may be carried out at pH 5.5 to 7 by weighing the ppt. The conversion factor to Zn is 0.1012. The sensitivity is 20 or 30  $\mu g$  of Zn per ml. In the presence of large amounts of ammonium salts, high results are obtained, and it is necessary in this case to ignite the ppt. to ZnO. Illustrations of the crystals of the compound of Zn with I (black crystals in clusters) are given.

C. D. KOPKIN

4. 5-(Indol-3-ylmethylene)rhodanine and the three isomeric 5-(pyridylmethylene)rhodanines, and their behaviour as organic reagents. R. Neu (Chem. Forsch.-Lab. der Dr. W. Schwahe, G.m.b.H., Karlsruhe, Germany). *Chem. Ber.*, 1957, 90, 2638-2643.—The preparation of these rhodanines

is described together with their use in the detection and separation of  $Cu^I$ ,  $Cu^{II}$ ,  $Hg^I$ ,  $Hg^{II}$  and Ag.

C. A. SLATER

5. New fluorescent indicators. I. Neutralisation titrations. Z. Holzbecher (Inst. Anal. Chem., High-School Chem. Technol., Prague). *Chem. Listy*, 1958, 52 (3), 425-429.—The following condensation products of salicylaldehyde were found to be very suitable fluorescent indicators in neutralisation titrations—the acetylhydrazone, semicarbazone and thiosemicarbazone of salicylaldehyde, *o*-hydroxyphenylbenzothiazole, *o*-hydroxyphenylbenzoxazole and *o*-hydroxyphenylbenziminazole. The dissociation constants and fluorescence changes are given for 13 compounds studied. Procedure for acids.—To the acid in a 150-ml titration vessel add an ethanolic soln. of the indicator (1 to 2 drops) (0.1%), dilute to  $>25$  ml and titrate with 0.1 N NaOH in u.v. light; the first fluorescence indicates the end-point. Compare with a blank. Hydrochloric, nitric, sulphuric, phosphoric and acetic acid were titrated with an average error of  $\pm 0.2\%$ .

J. ŽYKA

6. A new alkalimetric primary standard, sodium hydrogen diglycolate. D. A. Keyworth and R. B. Hahn (Chem. Dept., Wayne State Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1958, 30 (8), 1343-1344.—Sodium hydrogen diglycolate is readily prepared from commercial diglycolic acid, and can be purified by recrystallisation from water. Full details of preparation and purification are given. The solubility is 5.1 g per 100 g of water at 25°; the soln. has a pH of 3. The compound is readily dried (2 hr. at 120°), and is then very stable in air. End-point detection is excellent with phenolphthalein. Because of ease of purification and stability, the compound is stated to have advantages over K H phthalate.

F. L. SELFE

7. Analytical reactions of *tert*-butyl hypochlorite. C. E. Van Hall and K. G. Stone (Michigan State Univ., E. Lansing, U.S.A.). *Anal. Chem.*, 1958, 30 (8), 1416-1418.—The preparation and properties of a standard soln. of *tert*-butyl hypochlorite in acetic acid are described and its value as an oxidising titrant in non-aq. soln. is assessed. Styrene can be titrated amperometrically or potentiometrically in the presence of LiCl. The use of *tert*-butyl hypochlorite for determining other unsaturated compounds has been studied, but no satisfactory results have been obtained.

G. BURGER

8. Application of a colorimetric end-point to iodate procedures in presence of mercuric mercury. M. G. Bapat and S. V. Tatwawadi (Chem. Lab., Hindu Univ., Benares, India). *Anal. Chim. Acta*, 1958, 18 (4), 334-338.—The reduction of  $IO_3^-$  to  $I^-$  is facilitated by addition of  $Hg^{2+}$ , which forms a stable complex,  $[HgI_4]^{2-}$ , at low acidity. At high acidity this is decomposed and the liberated  $I^-$  are oxidised by excess of  $IO_3^-$ , first to I and then to

I<sup>+</sup>. The colour changes due to liberation and complexing or oxidation of I are followed in a Spekker absorptiometer with a blue filter transmitting in the range 450 to 500 m $\mu$ . An aliquot of iodate soln. (2 to 6 ml) is taken in the cell, treated with 2 ml of satd. aq. HgCl<sub>2</sub> acidified to 1.5 to 2.5 N with HCl, and titrated with a reductant. As the titration proceeds, the extinction falls to a minimum half-way through, then rises to its original value at the first equivalence point. In the reverse titration, when reductant is titrated with IO<sub>3</sub><sup>-</sup>, the extinction remains at a max. to the end-point, which is marked by a fall. The acidity is then raised from 2 to 6 N, when further addition of IO<sub>3</sub><sup>-</sup> causes the extinction to fall to a minimum, then rise to a constant max. at the second (ICl) end-point. Results are given for the determination of As<sup>3+</sup>, hydrazine and S<sub>2</sub>O<sub>3</sub><sup>2-</sup>; SCN<sup>-</sup> can be determined indirectly by adding excess of IO<sub>3</sub><sup>-</sup> and back-titrating with standard As<sub>2</sub>O<sub>3</sub> soln. As little as 5 mg of the reductants could be determined with an accuracy of 97 to 98%.

R. E. ESSERY

9. **Precipitation exchange reactions.** L. Erdey and E. Bányai (Tech. Univ., Budapest). *Z. anal. Chem.*, 1958, **161** (1), 16-28.—An exchange reaction occurs when a suspension of a sparingly soluble salt is mixed with an electrolyte, one of whose ions forms with it an even less soluble compound. The ion that is pptd. can be determined by titrating the liberated ion. The completeness of the reaction is denoted by the ratio of the end concn. of the liberated ion to the original concn. of the ion to be determined. This ratio, which is dependent on pH and molarity, can be calculated from the solubilities and dissociation constants or determined experimentally. The calculated results are in good agreement with experimental results and serve to assess the value of exchange reagents for quant. analysis. Of the commonly used reagents, AgIO<sub>3</sub> is shown to be the most suitable for the determination of Cl<sup>-</sup>; BaCrO<sub>4</sub> and Ba oxalate are both more satisfactory than Ba(IO<sub>3</sub>)<sub>2</sub> for SO<sub>4</sub><sup>2-</sup>; and Ag oxalate and Pb oxalate offer sensitive and precise methods for S<sup>2-</sup>.

G. BURGER

10. **Floril as an adsorbent for basic substances.** A. Asatour and C. E. Dalglish (Postgrad. Med. Sch., Duane Rd., London). *J. Chem. Soc.*, 1958, 1717-1718.—Adsorption characteristics of several basic substances under standardised experimental conditions are tabulated.

H. F. W. KIRKPATRICK

11. **Semi-quantitative gas chromatography.** R. H. Eastman (Dept. of Chem. and Chem. Engng, Stanford Univ., Calif., U.S.A.). *J. Amer. Chem. Soc.*, 1957, **79**, 4243.—With He as carrier gas and a tungsten wire detector it is found that

$$(m_i/W) = (A_i \sqrt{M_i}) / (\sum A_i \sqrt{M_i})$$

where  $m_i/W$  is the fraction by weight of the  $i$ th component,  $A_i$  is the area of the peak on the chromatogram corresponding to the  $i$ th component and  $M_i$  its mol. wt. The equation is applicable only to mixtures that are completely resolved and such that all components appear in the chromatogram.

C. A. SLATER

12. **Displacement development on ion exchangers. Separation of two ions.** J. Coursier and J. Hure (Dépt. de Métall. et de Chim. Appl., Commissariat à l'Energie Atomique, Saclay, France). *Anal.*

*Chim. Acta*, 1958, **18** (4), 272-281 (in French).—A mathematical discussion is given, covering the equilibrium of two ions between an exchange resin and the soln., frontal analysis for two and three ions, and displacement development. From the equilibrium constants, the phenomena encountered in the frontal analysis of two ions can be predicted, and thence the separation of two compounds by displacement development, including the prediction of the minimum distance which a band must travel to secure a separation of the compounds in zones. The method is illustrated by results for the separation of a mixture of Na<sup>+</sup> and K<sup>+</sup>, with Dowex 50 as ion exchanger and Ca<sup>2+</sup> as developer.

R. E. ESSERY

13. **A note on the periodic acid-Schiff reaction.** J. Barrolier, E. Watzke and K. H. Hölzer (Hauptlab. der Schering A.-G., Berlin-West). *Naturwissenschaften*, 1956, **43** (17), 398-399.—Well-stained bands on a pure white background are obtained with this more elaborate method. The fuchsin is first purified on a column of neutral alumina by the use of ethanol-chloroform (1:1); the second zone contains the pure fuchsin. The staining reagents are—(i) freshly prepared 1% aq. periodic acid; (ii) fuchsin reagent—0.5 g of purified fuchsin is dissolved in 100 ml of hot water and, after cooling the soln. to 50°, 1 g of NaHSO<sub>3</sub> and 36 ml of N HCl are added; after 2 hr. the soln. becomes decolorised, then 0.5 to 1.0 g of activated charcoal is added and the reagent is filtered; (iii) sulphite reagent—1 g of NaHSO<sub>3</sub> is dissolved in 100 ml of water containing 0.6 ml of glacial acetic acid; (iv) 90% ethanol (denatured) containing 4 ml of N HCl per 100 ml. *Procedure*—The electropherograms are dried at 85° and buffer salts are removed by washing in 66% aq. acetone. The strips are dried and immersed in (i) for 4 min., then washed in three changes of water and transferred to a bath of (ii) for 8 min., which is followed by washing in (iii) for 6 min. [(iii) should be renewed three times during this period]. This is followed by washing in running tap water. The background will still show some colour at this stage; final decolorisation of the background is achieved by washing in (iv). Acetylated paper gives the best results.

E. KAWERAU

14. **Errors in infra-red absorption analysis due to solute-solvent interactions.** W. R. Ward and A. R. Philpotts (Development Dept., Brit. Ind. Solvents, Salt End, Hedon, Hull). *J. Appl. Chem.*, 1958, **8** (4), 265-267.—Considerable errors can be incurred in quant. analyses owing to interactions of solute and solvent. The nature of the interaction is not known, but may be due to weak mol. associations or to perturbations of the absorbing mol. by neighbouring mol. Several methods are available for reducing the magnitude of these errors. Calibration curves may be constructed which take into account the effect of the solvent. Integrated optical density may be determined instead of peak optical density. Variation of the solute to solvent ratio may help, or comparison with a matched soln. is a reliable but somewhat slow method.

G. S. ROBERTS

15. **Stable turbidity standard for nephelometric quantitative analysis.** B. A. Fikhman. *Lab. Delo*, 1958, **4** (2), 53-55.—A stable turbidity standard is prepared from Soviet borosilicate glass (GOST 62-3652; composition—SiO<sub>2</sub> 80%, Fe<sub>2</sub>O<sub>3</sub> plus Al<sub>2</sub>O<sub>3</sub> 2%, B<sub>2</sub>O<sub>3</sub> 12%, Na<sub>2</sub>O  $\approx$  4% and K<sub>2</sub>O > 1%).



Pieces of glass (0.5 to 1 cm) are shaken for 4 hr. in a machine with 4 vol. of water. The liquid fraction is then discarded and the residual particles are washed and dried. The dry particles are sterilised by heating to 160° for 2 hr. Water containing thiomersalate (1 in 10<sup>4</sup>) is added to make the vol. up to the original and the flask is then shaken in a machine for 6 hr. on each of 4 successive days. The cloudy suspension is decanted and freed from large particles by setting aside for 24 hr. The liquid is re-decanted and the suspension obtained forms the base for the standard. The particles remain in suspension for 3 weeks, but they can be re-dispersed without changing the turbidity.

E. HAYES

**16. Polarographic methods with special reference to trace analysis.** H. A. McKenzie (C.S.I.R.O., Biochem. Dept., Univ. Sydney). *Rev. Pure and Appl. Chem.*, 1958, **8** (1), 53-84.—A review, with 169 references.

See also Abstracts—**34, 35**. Furfil  $\alpha$ -monoxime as reagent for Cu. **36**, Bismuthiol II as reagent for Cu. **77**, *o*-Salicylideneaminophenol and salicylaldehyde acetylhydrazone as fluorescent indicators. **128**, Trihydroxyaurine as reagent for metavanadate. **134**, 4-Amino-4'-chlorodiphenyl as reagent for SO<sub>4</sub><sup>2-</sup>. **169**, Tris-(*o*-hydroxyphenyl)-phosphine oxide as reagent for Fe<sup>3+</sup>.

## 2.—INORGANIC ANALYSIS

General determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

**17. Chemical microscopy. Metal chloride-quinoline compounds.** J. M. Mutchler and H. B. Bradley (Tonawanda Res. Lab., Linde Co., Div. of Union Carbide Corp., N.Y.). *Anal. Chem.*, 1958, **30** (8), 1371-1374.—Solid chlorides of bivalent Co, Cu, Fe, Mn, Hg, Ni, Cd, Ca, Zn and In, and of univalent Cu and Tl react with quinoline to form characteristic crystalline compounds, which may be differentiated by means of the polarising microscope. The crystal characteristics are tabulated and illustrated.

F. L. SELFE

**18. Action of phenols on a series of ions.** S. Ya. Shnalderman and I. B. Roberova. *Izv. Kievsk. Politekh. Inst.*, 1957, **20**, 108-126; *Ref. Zhur.*, *Khim.*, 1958, Abstr. No. 39,341.—The reactions of Fe<sup>3+</sup>, Ti<sup>4+</sup>, VO<sub>3</sub><sup>-</sup>, MoO<sub>4</sub><sup>2-</sup> and Ce<sup>4+</sup> with phenol, catechol (I), resorcinol, phloroglucinol, gallic acid (II), thymol, quinol, pyrogallol (III), and 1- and 2-naphthol, using a photocolorimeter with a blue filter, are studied. One ml of 0.1, 0.01 or 0.001 M soln. of the ions indicated was mixed with 1 ml of 0.1 M soln. of the reagents enumerated, in the presence of 8 ml of buffer soln. of pH 1 to 10 (for pH 1 to 3 mixtures of HCl and KCl were used, and for pH 3 to 10 ammoniacal acetate buffer soln. were employed). It is established that the ions studied form intensely coloured soluble products with only I, II and III. The high sensitivity of the reaction with these reagents is explained by the formation of internally complexed salts because of the presence in the molecules of I, II and III of two hydroxyl groups in the *ortho*-position. The dependence of the colour of the reaction products and its intensity on the pH of the soln. and the ratio of concn. of ion and reagent is studied.

C. D. KOPKIN

**19. Infra-red spectra of metal anthranilates and their analytical use.** R. Neeb (Anorg. chem. Inst. der Univ., Mainz, Germany). *Z. anal. Chem.*, 1958, **161** (3), 161-178.—The anthranilates of the following metals were prepared and their infra-red spectra determined—Cu<sup>II</sup>, Fe<sup>II</sup>, Ni<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Mn<sup>II</sup>, Hg<sup>II</sup>, Ag, Pb<sup>II</sup>, Na, Ba<sup>II</sup>. In general, the spectra resemble that of anthranilic acid, but, in the 9 to 10- $\mu$  region, bands occur that are characteristic of the metal cation. The wavelength at which these bands occur is in each case proportional to the stability of the chelate complexes of the metal, and also its second ionisation potential. The wavelengths of some of the characteristic bands are—Cu<sup>II</sup> 8.95 to 9.0  $\mu$ , Ni<sup>II</sup> 9.35  $\mu$ , Zn<sup>II</sup> 9.45 to 9.50  $\mu$ , Co<sup>II</sup> 9.62  $\mu$ , Cd<sup>II</sup> 9.75  $\mu$ , Fe<sup>II</sup> 9.84  $\mu$ , Mn<sup>II</sup> 10.0  $\mu$ . It is possible to analyse a mixture of two metals by pptg. the anthranilates and obtaining the characteristic band maxima, which are a measure of the ratio of the components, from the infra-red spectrum of the anthranilate mixture. From the total amount of the metals present, which is determined gravimetrically, it is then possible to determine the composition of the mixture. The method is described and exemplified in detail for the mixtures Cu-Zn, Cd-Zn and Cu-Cd. The main sources of error are discussed. The total error is in the region of  $\pm 3\%$ , which is comparable with that of colorimetric methods. Total analysis may be carried out by the method, by measuring the ratio of the components in the mixture and also the total metal compounds present from the spectrum of the anthranilate mixture. Results are satisfactory only for those elements that are extremely difficult to analyse by other methods.

S. M. MARSH

**20. Use of organic phosphorus compounds in inorganic analysis.** I. P. Ryazanov and I. P. Khazova. *Sb. Nauch. Trud. Magnitogorskii Gorno-Metallurg. Inst.*, 1957, (13), 29-35; *Ref. Zhur.*, *Khim.*, 1958, Abstr. No. 53,393.—The analytical properties of *o*-nitrophenylphosphinic acid (I), dimethylaminophenylphosphonous acid (II) and 5:10-dihydro-10-hydroxyphenophosphazine (III) are studied. It is established that I is a specific reagent for Ag<sup>+</sup> and Hg<sub>2</sub><sup>2+</sup>. The solubility of the ppt. formed by I with Ag<sup>+</sup> is 5.7  $\times 10^{-3}$  moles per litre, with a detectable minimum of 0.25  $\mu$ g of Ag<sup>+</sup>; limiting dilution 1 in 8  $\times 10^4$ . II forms ppt. with Ca<sup>2+</sup>, Ba<sup>2+</sup> and Pb<sup>2+</sup>, the solubilities of which are respectively 6.7  $\times 10^{-3}$ , 6.1  $\times 10^{-3}$  and 6.3  $\times 10^{-3}$  moles per litre; detectable minimum 20, 7 and 5  $\mu$ g; limiting dilution 1 in 2.5  $\times 10^3$ , 1 in 10<sup>3</sup> and 1 in 10<sup>3</sup>. III forms difficultly soluble ppt. with Ti<sup>4+</sup> (pale yellow-pink soluble in ethanol, insoluble in dilute mineral acids, detectable minimum 3.3  $\mu$ g, limiting dilution 1 in 1.5  $\times 10^4$ ), with UO<sub>2</sub><sup>2+</sup> (yellow, soluble in ethanol, insoluble in mineral acids, detectable minimum 6.8  $\mu$ g, limiting dilution 1 in 7.3  $\times 10^3$ ) and with Hg<sub>2</sub><sup>2+</sup> (white, gradually darkening because of reduction of Hg<sub>2</sub><sup>2+</sup> to metallic Hg); it also reduces Ag<sup>+</sup> to metallic Ag. The synthesis of I, II and III is described.

C. D. KOPKIN

**21. Anion adsorption of some metals from a mixture of hydrochloric acid and methanol.** Masuo Kojima (Chem. Dept., College of Gen. Educ., Tokyo Univ., Meguro-ku). *Japan Analyst.*, 1958, **7** (3), 177-180.—The *K<sub>d</sub>* (partition coeff.) value of the chloro complexes of Fe<sup>III</sup>, Cu and Co towards Dowex 1-X8 increases with increasing concn. of methanol in HCl. At a given concn. of methanol,

the  $K_d$  value increases monotonically with increase in concn. of HCl. This is applied to the separation of Ni, Co, Cu, Fe and Zn. Nickel is not adsorbed on the column (diam. 10 mm, length 10 cm; 120 to 200 mesh) from 3.5 N HCl in 60% methanol; Co, Cu, Fe and Zn are successively eluted with 2.5 N HCl in 60% methanol, 3 N HCl in 30% methanol, N HCl in water, and water, respectively. For the separation of Ni, Co and Fe, the elution is made more rapid by the respective use of 2 N HCl in 80% methanol, 2 N HCl in 60% methanol, and N HNO<sub>3</sub>.

K. SAITO

**22. Focusing ion exchange. V. Separation of metal ions, especially of radioactive indicators, by exchange with protons.** E. Schumacher and H. J. Streiff (Chem. Inst., Zurich Univ., Switzerland). *Helv. Chim. Acta*, 1958, **41** (3), 824-843.—Focusing ion exchange (cf. Schumacher, *Anal. Abstr.*, 1957, **4**, 2078) is studied by using a pH gradient to produce a gradient in chelating tendency. An apparatus for separation on paper strips is described. Optimum conditions are found for the separation of test mixtures (Co and Cu; and Ba, Sr and rare earths) and some applications of the method are mentioned.

M. DAVIS

**23. Paper chromatography of cations.** E. S. Bolchinova and V. S. Khëifets. *Trudy Leningr. Tekhnol. Inst. im. Lensovetu*, 1957, (43), 12-19; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,396.—Successful experiments have been carried out on the separation of mixtures of the cations of the third and fourth analytical groups by ascending chromatography on strips of ordinary filter-paper, with elution with a mixture of butanol and conc. HCl (4:1). The same values of  $R_F$  are obtained as on special chromatographic paper; it is established that the value of  $R_F$  depends on the composition of the solvent. The value of  $R_F$  for Mn<sup>2+</sup> is 0.10.

C. D. KOPKIN

**24. Chromatographic separation on paper of certain ions of widely different elements.** E. S. Bolchinova and L. B. Zommer. *Trudy Leningr. Tekhnol. Inst. im. Lensovetu*, 1957, (43), 20-22; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,398.—The possibility is studied of separating mixtures of ZrO<sub>2</sub><sup>2+</sup>, WO<sub>4</sub><sup>2-</sup>, TiO<sub>2</sub><sup>2+</sup>, VO<sub>3</sub><sup>-</sup>, Fe<sup>3+</sup> and MoO<sub>4</sub><sup>2-</sup> by paper chromatography. Best results were obtained with elution with a mixture of butanol and 3 N HCl (4:1, by vol.). The use of acetic acid or butyl acetate with butanol and water gives a worse separation. The ions ZrO<sub>2</sub><sup>2+</sup> and WO<sub>4</sub><sup>2-</sup> remain at the point of introduction and are only slightly separated by elution with a soln. of 0.5 g of tartaric acid in 100 ml of butanol.

C. D. KOPKIN

**25. Separation of heavy-metal ions from mixtures with boric acid by ion-exchange resin.** A. K. M. A. Huq, S. K. Deb and M. H. Khundkar (Chem. Dept., Univ. of Dacca, East Pakistan). *J. Indian Chem. Soc., Ind. Ed.*, 1958, **20** (3-4), 127-130.—A sulphonic acid cation-exchange resin (Zeo-Karb 225) is used to separate Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup> or Ag<sup>+</sup> from mixtures with boric acid, and offers a simple method for the quant. determination of boric acid in such mixtures. The adsorbed metal ions may be eluted later under suitable conditions and determined quantitatively.

I. JONES

**26. Potentiometric titrations with (ethylene-dinitrilo)tetra-acetate [EDTA]. Use of masking agents to improve selectivity.** J. S. Fritz, M. J. Richard and

S. K. Karraker (Dept. of Chem., Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1347-1350.—The use of citrate, sulphosalicylate and acetylacetone as masking agents has been investigated and results are reported. Titrations of metal ions with EDTA (disodium salt) are carried out with the use of a mercury indicator electrode. By using citrate at a pH of 6.5 to 7.5, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> can be titrated in the presence of any of the following—Th<sup>4+</sup>, Zr<sup>4+</sup>, Ti<sup>4+</sup>, Sn<sup>4+</sup>, Fe<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup>, Cr<sup>3+</sup>, Be<sup>2+</sup>, Sb<sup>3+</sup>, Nb<sup>5+</sup>, Ta<sup>5+</sup>, Mo<sup>6+</sup> and W<sup>6+</sup>. The lower rare earths and Ag<sup>+</sup>, Al<sup>3+</sup>, Bi<sup>3+</sup> and Ga<sup>3+</sup> are incompletely masked and interfere; Y<sup>3+</sup> and the higher rare earths can be titrated in the presence of Mo<sup>6+</sup>, Sn<sup>4+</sup>, Th<sup>4+</sup> or Ti<sup>4+</sup>, but this titration fails when Be<sup>2+</sup>, Fe<sup>3+</sup>, Nb<sup>5+</sup> or Ta<sup>5+</sup> are present. By using sulphosalicylate at a pH of 4.5 to 5.0, Al<sup>3+</sup> and U<sup>6+</sup> are masked effectively, enabling the rare earths, Y<sup>3+</sup>, Th<sup>4+</sup> and some bivalent metals to be titrated. Acetylacetone, at a pH of 6.5 to 7.5, is most useful in masking Al<sup>3+</sup> or U<sup>6+</sup> during the titration of rare earths. Zinc can be titrated in the presence of both Th<sup>4+</sup> and Al<sup>3+</sup> by using citrate to mask Th and acetylacetone to mask Al. Mention is made of the use of tartrate and fluoride as masking agents.

F. L. SELFE

**27. Drop-time method of conductimetric titration of certain ions.** A. K. Kal'e and M. I. Kulikov. *Trudy Gor'kovsk. Politekh. Inst.*, 1957, **13** (5), 47-49; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,402.—The earlier described drop-time method of conductimetric titration (Kal'e, *Zavod. Lab.*, 1946, **12**, 773; 1947, **13**, 413) is used for the determination of Fe<sup>3+</sup> and Cu<sup>2+</sup>; aq. NH<sub>3</sub> is used as titrating reagent. It is established that in the titration of Fe<sup>3+</sup> the inflection point coincides with the equivalence point of Fe(OH)<sub>3</sub>. To determine Fe<sup>3+</sup> or Cu<sup>2+</sup>, add 50 or 60 ml of water to the soln., stir and titrate automatically with 0.1 N aq. NH<sub>3</sub> from a Mariotte vessel. The curve of the dependence of time (in sec.) on concn. up to the inflection point is a straight line inclined at 45°. In the case of Cu<sup>2+</sup> (12 to 60 mg) the straight line has a greater slope and does not pass through the origin. The error of the determinations is  $\pm 0.2$  mg; one titration takes 6 or 7 min.

C. D. KOPKIN

**28. Amperometric titration with oxalate.** Yu. I. Usatenko and M. A. Vitkina. *Ukr. Khim. Zhur.*, 1957, **23** (6), 788-791; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,370.—The oxidation of the oxalate ion at the rotating platinum electrode is studied. It is established that the current-voltage curves for soln. of ammonium oxalate in a basal soln. of 0.1 N KNO<sub>3</sub> have two plateaux, corresponding to the stepwise oxidation of the oxalate ion; the first is at 0.4 to 0.5 V, the second at 0.85 to 1.1 V. The second plateau is the sharper, so that the quantitative determination is carried out with an applied e.m.f. of 0.9 to 1.0 V. The oxidation of the ion takes place only at pH 3.6 to 4.7. Under these conditions a direct proportionality between the height of the wave and the concn. of the ion within the limits  $2 \times 10^{-4}$  to  $2 \times 10^{-6}$  M is observed. On this basis it is proposed that standard soln. of ammonium oxalate be used for the amperometric determination of elements that form insoluble ppt. or stable soluble complexes with oxalate. Optimum conditions are established for the amperometric titration with a soln. of ammonium oxalate of Hg (1 to 10 mg in 50 ml of soln. at pH 3.6); Ag (5 to 10 mg in 50% ethanolic soln.); Pb (5 to 50 mg in 50 ml of soln. at pH 4.05); Ca (2 to 20 mg

in 50 ml of soln. at pH 3.7 to 4.0) and Fe (at pH 3.6 to 4.7). The end-point of the determination is recognised by the appearance of the anode diffusion current. The error of the determination is  $\pm 5\%$ .

C. D. KOPKIN

**29. Radiochemical analysis for long-lived fission products in environmental materials.** W. F. Merritt (Health Physics Branch, Atomic Energy of Canada Ltd., Chalk River, Ontario). *Canad. J. Chem.*, 1958, **36** (3), 425-428.—A method of determining  $^{106}\text{Ru}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$  and  $^{144}\text{Ce}$  is described. A standardised carrier soln. (20 mg of Sr, Ce and Cs, and 10 mg of Ru) is added to suitable quantities of the test material. The mixture is neutralised and dried, then fused with  $\text{KOH-KNO}_3\text{-K}_2\text{CO}_3$  (2:1:1, by wt.) at  $550^\circ$  for 2 hr. After cooling, the melt is leached with water, which dissolves the Cs and the ruthenate formed by oxidation. The ruthenate is oxidised, by addition of  $\text{KIO}_4$ , to  $\text{RuO}_4$ , which is then extracted from the aq. soln. with  $\text{CCl}_4$ . The residual aq. layer is treated with satd.  $\text{LiOH}$  soln., filtered, and then passed through a Duolite C-3 resin column. After elution of  $\text{K}^+$  and  $\text{Li}^+$  with 0.5 N  $\text{LiOH}$  and 0.2 N  $\text{HCl}$ , respectively, the Cs is stripped off the column with 6 N  $\text{HCl}$ . The residual solids from the original melt are extracted with 6 N  $\text{HNO}_3$ . After removal of the silica, Ce is pptd. with  $\text{NH}_3$  gas as  $\text{Ce}(\text{OH})_3$ , and filtered off. The Sr in the filtrate is then pptd. by the addition of  $\text{Na}_2\text{CO}_3$ . The radioactive counts are made on the ppt. according to standard procedures.

P. M. SORGO

**30. Spectrographic quantitative analysis of the isotopic composition of gaseous mixtures of hydrogen, deuterium and tritium.** M. N. Oganov and A. R. Striganov. *Atomn. Energiya*, 1957, **3** (8), 112-120; *Ref. Zhur., Khim.*, 1958, Abstr. No. 14,211.—The spectra are recorded with a glass three-prism spectrograph with an auto-collimating camera at a dispersion of 9.5 Å per mm at 6500 Å. The lines due to  $\text{D}_2$  and  $\text{T}_2$  are not completely resolved at this dispersion. Illuminate the slit with a condenser lens of  $F$  1200 mm with sharp focusing of the light source on the objective. Use a three-step sector on the slit. Excite the spectra in a quartz non-electrode tube with a capillary of diam. 1.5 mm by means of a H.F. generator of 800 W, frequency 10 megacycles at a current strength in the tube of 400 milliamp. A special vacuum apparatus is described for the preparation of standard gas mixtures, working on the principle of partial pressures at const. vol. The preparation of the standards is described in detail. For the analysis, the lines due to  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{T}_2$  are used. Before the analysis, de-gas the tube, wash it with the sample, commence the discharge and then fill with the samples at a pressure of 0.4 mm (Hg). Photograph the spectra on panchromatic plates with an exposure of 3 to 6 sec. An analysis is made of the calibration curves for a wide range of concn. It is established that equal intensity of the lines due to H and D is achieved at a ratio of  $C_H$  to  $C_D$  of 1.13, where  $C$  is the concn. of gas molecules, which is explained by the authors by the different dissociation energies of the  $\text{H}_2$  and  $\text{D}_2$  molecules and by the different Doppler widening of the lines. It is observed that the ratio of  $I_H$  to  $I_D$  depends on the pressure in the discharge tube, for, according to the authors, the same reasons. The error of the analysis at high concn. of H (up to 89%) is  $\pm 0.6\%$ ; with decrease in the content of H to a few per cent. the error increases to 5 or 6%.

C. D. KOPKIN

**31. Quantitative separation of helium - neon mixtures.** G. M. Ermolin. *Trudy Radiov. Inst., Akad. Nauk, SSSR*, 1957, **6**, 119-138; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,374.—The method described is based on the different adsorptive ability of activated charcoal towards He and Ne under conditions close to the critical temp. of Ne ( $-228.7^\circ$ ). Under these conditions there is almost complete adsorption of Ne by activated carbon of type "AG"; the average adsorption of He under these conditions is 5-1%. At temp.  $\approx -225^\circ$ , Ne is not quant. adsorbed; on the average 0.63% is not adsorbed. In the direct determination of He, it is necessary to introduce a constant correction of 5.4% for adsorption of He at  $-228.7^\circ$ , and a correction of 0.63% for the presence of residual Ne above the activated charcoal "AG" at  $-225^\circ$ . In the direct determination of Ne, the correction for that not adsorbed should be introduced only when the amount of Ne is small (less than in air) and when the Ne is determined at  $-225^\circ$ . New data have been obtained for the content of He and Ne in air, namely He 0.000474% and Ne 0.001766%. The results are considered to be the most accurate at the present time (max. error  $\pm 2\%$ ).

C. D. KOPKIN

**32. Separation of lithium and sodium by displacement development on ion exchangers.** A. D. Jouy and J. Coursier (Lab. de Chim. Anal., École Sup. de Phys. et de Chim., Paris, France). *Bull. Soc. Chim. France*, 1958, (3), 323-325.—The ratio of distribution coefficients of  $\text{Li}^+$  and  $\text{Na}^+$  between the resin and an aq. soln. is determined by frontal analysis on a 200 to 400-mesh Dowex-50 column. This ratio is approx. constant with changing composition and has the value 1.95 ( $\pm 1\%$ ). Displacement development of a mixed soln. of  $\text{Li}_2\text{SO}_4$  (0.35 M) and  $\text{Na}_2\text{SO}_4$  (0.15 M) on a Dowex-50 column 110 cm long and 1 cm in diam. is effected with 0.5 M  $(\text{NH}_4)_2\text{SO}_4$ . It is shown that the main lithium fractions recovered contain  $< 1$  part in 10,000 of Na in one operation (observed with  $^{24}\text{Na}$ ).

E. J. H. BIRCH

**33. Polarographic analysis of heavy metals in reagent-grade sodium chloride. II. Determination of copper and zinc.** Kishiro Sugihara and Toshihide Saito (Osaka Ond. Res. Inst., Ooyodo-ku, Osaka). *Japan Analyst.*, 1958, **7** (3), 139-142.—Copper ( $< 0.0001\%$ ) and Zn ( $< 0.0001\%$ ) in reagent-grade  $\text{NaCl}$  are extracted (together with Pb) with dithizone in  $\text{CCl}_4$  at pH 9 (*Anal. Abstr.*, 1955, **2**, 2381), then extracted back with  $\text{HCl}$  and determined polarographically in tartrate and  $\text{KSCN}$  soln., respectively, as supporting electrolytes. Approx. 95% of Cu and 100% of Zn are extracted. The wave height is proportional to concn. in the range 1 to  $5 \mu\text{g}$  of Cu and 0.2 to  $1.5 \mu\text{g}$  of Zn per ml.

K. SAITO

**34. New sensitive method for the detection of copper.** V. Armeanu and C. Iancu (Lab. of Inorg. and Anal. Chem., Univ. C.I. Parhon, Romania). *Stud. Cercet. Chim., Acad. R.P.R.*, 1957, **5** (3), 423-430.—The reaction of furil  $\alpha$ -monoxime with Cu (*cf. Feigl et al., Ber.*, 1925, **7**, 2294) has been modified. A drop of a copper soln. is dried on filter-paper over a flame; a drop of an alcoholic soln. (1%) of the reagent is added and the soln. is exposed to  $\text{NH}_3$  vapour. A green stain surrounded by a brown ring is formed which is stable for months. It is claimed that the detection limit is  $0.011 \mu\text{g}$  of Cu, and the limit of dilution is in  $5 \times 10^4$ . The sensitivity is impaired if the test is carried out otherwise,

e.g., in a micro-tube, on a cover-slip or on porcelain. Bivalent Co and Ni<sup>2+</sup> give pale-brown and coffee-coloured ppt., respectively, and Fe<sup>3+</sup> give an intense red soln. Under the test conditions, Pb<sup>2+</sup>, Ag<sup>+</sup>, Hg<sub>2</sub><sup>2+</sup>, Hg<sup>2+</sup>, Bi<sup>3+</sup>, Cd<sup>2+</sup>, AsO<sub>4</sub><sup>3-</sup>, AsO<sub>3</sub><sup>3-</sup>, Sb<sup>3+</sup>, Sn<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup> give no reaction. H. SHER

**35. New macro- and micro-methods for the gravimetric determination of copper.** V. Armeanu and C. Iancu (Lab. Chim. Anorg. Anal., Univ. "C.I. Parhon," Romania). *Stud. Cercet. Chim., Acad. R.P.R.*, 1957, **5** (3), 431-435.—The method is based on the formation of the complex C<sub>10</sub>H<sub>7</sub>O<sub>4</sub>NCu by the reaction of Cu<sup>2+</sup> with furil  $\alpha$ -monoxime (I). **Macro-method**—A soln. containing an equivalent of  $\approx 0.15$  g of CuSO<sub>4</sub> is neutralised with HCl, NaOH or aq. NH<sub>3</sub>, diluted to 70 to 80 ml, and buffered with 2 g of ammonium acetate. It is heated to between 70° and 80°, and a minimum excess of an alcoholic soln. (1%) of I is added drop by drop with vigorous agitation. The ppt. is filtered off and washed with 1 to 2 ml of acetone ( $\times 6$  to 10) until the filtrate is colourless, then with 1 ml of anhydrous ether ( $\times 2$  to 3), and vacuum-dried for 5 to 10 min. **Micro-method**—The soln. should contain a max. of 4 mg of CuSO<sub>4</sub>·5H<sub>2</sub>O in 5 to 8 ml, and is treated as above, 0.01 g of ammonium acetate being used with 10 to 15 drops of the reagent. H. SHER

**36. Bismuthiol II as an analytical reagent. X. Estimation of copper.** A. K. Majumdar and B. R. Singh (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1958, **161** (2), 81-86 (in English).—With bismuthiol II (5-mercapto-3-phenyl-2-thio-1:3:4-thiadiazolone) (I), Cu forms a cupric complex of composition Cu(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>S<sub>3</sub>)<sub>2</sub>, which is stable up to 250°, melts at 148°, and is soluble in EDTA and in some organic solvents, and a cuprous complex of composition Cu<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>S<sub>3</sub>, which is stable up to 300°, melts at 198°, and is insoluble in EDTA and in organic solvents. Both complexes are stable in dil. acids. To determine Cu as the cupric complex, I is added to a hot acid soln. of the cupric salt and the ppt. is washed with warm H<sub>2</sub>O, dried and weighed. By the use of tartaric acid or KI as masking agent and by suitable adjustment of the acidity between pH 6.2 and 0.1 N HCl or H<sub>2</sub>SO<sub>4</sub> or 0.5 N acetic acid, interference by other ions, except those of Pd, Cd, Pb and Ti<sup>3+</sup>, can be prevented. To determine Cu as the cuprous complex, a sufficient excess of KI is added to the slightly acid copper salt soln. to dissolve the CuI formed, and the iodine liberated is reduced with aq. SO<sub>2</sub> soln. The soln. is heated and the cuprous complex pptd. by addition of I. The ppt. is washed with warm water, dried and weighed. If KCN is used in place of KI, Pd remains in soln. The range of acidities for the pptn. is from pH 7 to 0.1 N mineral acid or 1 N acetic acid, and the permissible masking agents include EDTA. The only interferences that cannot be eliminated are those due to Bi and Ti<sup>3+</sup>. G. BURGER

**37. Conductimetric determination of copper by direct titration with sodium thiosulphate.** D. Ceaușescu (Inst. of Hygiene, Timisoara, Romania). *Stud. Cercet. Chim., Cluj*, 1957, **8** (3-4), 285-290.—In the indirect titration of Cu<sup>2+</sup> by the addition of NaSCN and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in excess and back-titration with iodine, the oxidation-reduction reaction results in a diminution of the number of anions in soln., since 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup> give S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, and 2Cu<sup>2+</sup> give

2Cu<sup>+</sup>, followed by the pptn. 2SCN<sup>-</sup> + 2Cu<sup>+</sup> → 2CuSCN. This is the basis of a direct conductimetric determination of Cu. Thus when Cu(SCN)<sub>2</sub> is titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the conductivity curve rises slowly; but when all the Cu<sup>2+</sup> have been reduced to Cu<sup>+</sup> and pptd., the curve rises more steeply, the two branches meeting at the end-point. Not only is the method direct, but the errors involved in the back-titration with iodine are avoided. H. SHER

**38. Determination of copper in sea water, silicate rocks and biological materials.** J. P. Riley and P. Sinhaseni (Dept. of Oceanography, Univ. of Liverpool, England). *Analyst*, 1958, **83**, 299-304.—Filtered sea water (900 ml) is treated with 5 ml of 25% hydroxylamine hydrochloride soln. and 10 ml of N Na acetate buffer soln. and shaken with 8 ml of diquinoxyl reagent (0.03 g of 2:2'-diquinoxyl in 100 ml of purified n-hexanol), and extraction of the separated aq. layer is repeated with 3 ml of the reagent. To the combined extracts is added 0.5 ml of ethanolic quinol (1%) and the vol. is adjusted to 10 ml with n-hexanol. The extinction is measured at 540 m $\mu$  and referred to a calibration graph. In the preliminary procedure, silicate rock is treated overnight with HNO<sub>3</sub> and HF and, after evaporation, the residue is fused with KHSO<sub>4</sub> and dissolved in water and HCl. Carbonate rocks are treated with HNO<sub>3</sub>, the soln. is evaporated to dryness, organic matter is removed by evaporation with HNO<sub>3</sub>, and the HNO<sub>3</sub> is removed by evaporation with HCl. The residue is dissolved in water and HCl. Biological matter is heated with HNO<sub>3</sub> until all organic matter is destroyed, then fumed with HClO<sub>4</sub> and the residue is dissolved in water. Beer's law is obeyed to at least 10 p.p.m. of Cu in the n-hexanol phase. The method gave a coeff. of variation of 2.5% with sea water containing 27  $\mu$ g of copper per litre. A. O. JONES

**39. Potentiometric determination of copper in the presence of zinc by the sulphide method.** V. M. Babenyshev. *Sb. Nauch. Trud. Kuibyshevsk. Ind. Inst.*, 1957, (7), 29-35; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,353.—To determine Cu in the presence of Zn, the drop potentiometric titration method [Kal'e, *Zavod. Lab.*, 1946, **12**, 773], with Na<sub>2</sub>S as titrating reagent, is used. **Procedure**—Insert the electrode pair (platinum-carbon) into the titration beaker containing 0.001 mg each of CuSO<sub>4</sub> and ZnSO<sub>4</sub> in 50 ml of water, stirring electrically. Open the tap of a Mariotte vessel and simultaneously start a stop-watch, which is stopped when the characteristic displacement of the galvanometer needle is observed, indicating the end-point. In titrating a soln. containing Cu and Zn with Na<sub>2</sub>S soln. two such displacements are observed; the time from the commencement of the titration to the first is used to determine Cu from a calibration curve (time in sec. against concn. in moles per litre) constructed from the titration curves of standard soln. of Cu; the time from the first displacement to the second is used for the determination of Zn from a similar calibration curve. If the soln. contains equal amounts of Cu and Zn, the data obtained coincide with the theoretical results. Less satisfactory results are obtained in the titration of Cu in the presence of large amounts of Zn. A direct proportionality between time and the concn. of Zn is observed only for soln. of concn.  $\approx 0.04$  mole per litre. The determination of large amounts of Zn after pptn. of Cu is not possible. The analysis takes 5 to 10 min. C. D. KOPKIN



40. **Colorimetric determination of copper in nickel electrolytes.** A. I. Busev, M. I. Ivanyutin and E. M. Felgina (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1958, **24** (3), 265-266.—The method is based on the use of OO-diethyl hydrogen phosphorodithioate (cf. Busev and Ivanyutin, *Anal. Abstr.*, 1957, **4**, 2096) which gives a complex with Cu soluble in  $\text{CCl}_4$ . To determine 0.005 to 0.05 g of Cu per litre of nickel electrolyte, the filtered sample (5 to 10 ml) in a 100-ml cylinder is shaken with 50 ml of water, 6 ml of  $\text{CCl}_4$  and 3 ml of a 0.001 M soln. of the nickel salt of the reagent. To 50 ml of water in a similar cylinder are added  $\text{CCl}_4$  and the reagent soln. and also 1 to 2 ml of 2 N  $\text{H}_2\text{SO}_4$ , together with increasing amounts of a standard soln. of Cu (0.02 mg per ml) until the colour intensity of the organic layer matches that of the sample. G. S. SMITH

41. **Potentiometric micro-determination of silver by means of triazoles.** L. N. Lomakina, N. I. Tarasevich and P. K. Agasyan (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1958, **24** (3), 270-273.—With silver wire and saturated mercurous sulphate electrodes, Ag is titrated potentiometrically with ammoniacal soln. of benzotriazole or bromobenzotriazole. G. S. SMITH

42. **Flame-photometric determination of silver in blister copper.** N. McN. Galloway (Chem. Lab., Roan Antelope Copper Mines Ltd., Luanshya, N. Rhodesia). *Analyst*, 1958, **83**, 373-374.—An amount of clean blister copper to give a final soln. containing  $\approx 50$  p.p.m. of Ag is dissolved in conc.  $\text{HNO}_3$ . Br is then added to oxidise S and, after 10 min., dil.  $\text{HNO}_3$  (1 + 1) is added and the liquid is boiled to remove Br and nitrous fumes. It is then treated with 100 ml of water and 5 ml of 20% NaCl soln., boiled for 10 min. and set aside overnight in the dark. The collected ppt. is washed with water and dil.  $\text{HNO}_3$  alternately to remove copper, then dissolved by successive treatments with aq.  $\text{NH}_3$  and hot 20%  $\text{HNO}_3$ , made up to a known vol. and used for the flame-photometric determination. The most suitable wavelength is 338 m $\mu$ , the flame background being then very small. For more accurate results, the background can be measured at 335 and 341 m $\mu$  and allowed for in the usual way. Results agreed with those of a cupellation method. None of the common metals interfere. A. O. JONES

43. **Colorimetric determination of gold with p-dimethylaminobenzylidenerhodanine.** Shigeo Hara (Osaka Ind. Res. Inst., Saidacho, Ikeda, Osaka). *Japan Analyst*, 1958, **7** (3), 147-151.—The red Au-p-dimethylaminobenzylidenerhodanine complex (max. absorption 570 m $\mu$ ) (Merejkovsky, *Bull. Soc. Chim. Biol.*, 1933, **15**, 1336) obeys Beer's law in 0.02 to 0.05 N HCl for 3 to 30  $\mu\text{g}$  of Au per 100 ml. The colour remains unchanged for 30 min. Iron (<300 mg) is masked with  $\text{NaPO}_4$  soln. (10%, 30 ml for 100 ml of the final soln.) and Ag (<220  $\mu\text{g}$ ) with NaCl (3 g for 100 ml). There is no interference from Cu. K. SAITO

44. **Application of organoarsenic compounds to inorganic analysis. I. o-Aminobenzenearsonic acid as an analytical reagent for detection and determination of small amounts of gold.** Tien-Chih Chen and Shuai-Kuan Yeh (Dept. of Chem., Nan-Kai Univ.). *Acta Chim. Sinica*, 1957, **23** (6), 479-484 (English summary).—This reagent (1% soln.) gives a red coloration or ppt. with Au. The limiting dilution

is 1 in  $8 \times 10^6$  when tests are carried out in a test-tube. Most of the ions that interfere can be removed by pH adjustment, or with complex-forming reagents. The colour intensity obeys the Beer-Lambert law. The extinction of the red colour reaches its maximum after 40 min., and in some cases after 90 min., according to the amount of Au in the soln. Heating accelerates the rate of colour development. Solutions of pH 4 are found to be satisfactory. Certain metal ions interfere.

45. **Use of the radioactivation method for the determination of micro quantities of gold in solutions.** A. I. Kulak. *Trudy Moskov. Khim.-Tekhnol. Inst. im. D. I. Mendeleev*, 1957, (24), 376-379; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,023.—A method is evolved for the determination of Au in soln. in amounts that cannot be determined by ordinary methods. Analysis of the soln. is carried out by three different methods—activation of the dry residue after evaporation of the soln., activation of Au co-pptd. from the soln. with  $\text{PbS}$ , and activation of Au co-pptd. from the soln. with Te. Soln. containing  $10^{-10}$ ,  $5 \times 10^{-10}$  and  $10^{-9}$  g of Au are used as standards. The radiochemical purity of the separated Au is tested by measurement of the half-life of  $^{199}\text{Au}$ . The error in the determination of  $\approx 10^{-10}$  g of Au is +20%. C. D. KOPKIN

46. **Determination of beryllium in metallurgical analysis.** M. Kett (Res. Inst. of Ores, Panenské Brežany, Czechoslovakia). *Hutn. Listy*, 1958, **13** (3), 250-251.—Beryllium can be separated from all elements by extraction with acetylacetone and determined colorimetrically with the use of aluminon. The method is suitable for most types of material, particularly for aluminium bronzes with a low content of Be. J. ŽYKA

47. **Analytical use of phenolcarboxylic acids of the triphenylmethane series. Determination of beryllium in minerals and alloys.** I. S. Mustafin and L. O. Matveev (N. G. Chernyshevskii Saratov State Univ.). *Zavod. Lab.*, 1958, **24** (3), 259-262.—The use of Solochrome brilliant blue B (called alberon by the authors since it is proposed as a reagent for both Al and Be) for the absorptometric determination of Be (cf. Wood, *Anal. Abstr.*, 1955, **2**, 1769, and other authors) is studied. To determine Be in bronze, the soln. of the sample (0.1 g) in 5 to 10 ml of dil.  $\text{HNO}_3$  (1:1) is evaporated to dryness, 2 to 3 ml of dil. HCl (1:1) is added and the soln. is re-evaporated to dryness. The residue is dissolved in 200 ml of dil. HCl (1:100) and a 0.5-ml aliquot is mixed with 8 ml of a buffer soln. (pH 4.4 to 4.8), 0.5 ml of a 5% soln. of EDTA (disodium salt) and 1 ml of a 0.1% soln. of the reagent in water. The extinction in a 0.5-cm layer is measured at  $\approx 570$  m $\mu$  after 5 to 10 min. In the presence of EDTA and at pH  $\approx 4.5$  there is no interference from Al, Fe, Mg, Ca, Mn and Cr. Two procedures for the determination of Be in beryl are described. G. S. SMITH

48. **Back-titration with mercuric nitrate in alkaline medium. Volumetric analysis of binary mixtures of alkaline earths, magnesium, zinc and cadmium.** H. Khalifa (II Chem. Inst., Vienna Univ., Austria). *Anal. Chim. Acta*, 1958, **18** (4), 310-314.—Back-titration with  $\text{Hg}(\text{NO}_3)_2$  soln. of the excess of EDTA in soln. of Zn, Cd or Ca at pH 8, 9, 10 and 11 proceeds to the point corresponding to the excess of EDTA. With soln. of Mg, Ba or Sr, the end-points at pH 8 and 9 correspond to



total EDTA, but with Mg and Sr at pH 10 and 11, and with Ba at pH 11, they again correspond to excess of EDTA. By titrating at pH 8 or 9 and again at pH 11, mixtures of either Zn, Cd or Ca with either Mg, Ba or Sr can be analysed. End-points are detected potentiometrically, with an amalgamated silver electrode vs. the S.C.E., with satd.  $\text{KNO}_3$  as the salt bridge, and an automatic recording titrator. Results for 0.01 M mixtures of Cd with Mg, Ba or Sr, and of Zn with Ba or Sr (all as nitrates) show satisfactory recoveries.

R. E. ESSERY

**49. Amperometric determination of magnesium with the rotating platinum electrode.** B. A. Shmelev and E. N. Danilova. *Sb. Nauch. Rabot. Moskov. Inst. Nar. Kh.*, 1957, (10), 335-342; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,379.—The method is based on the pptn. of Mg with  $\text{Na}_2\text{HPO}_4$ . The optimum conditions for the amperometric titration are pH 10.5, e.m.f. 1.9 V. To 20 ml of soln. to be analysed add 0.1 ml of ammoniacal buffer soln. (pH 10.5), introduce the rotating platinum electrode, connect the soln. via an agar-agar salt bridge to a calomel reference electrode, apply an e.m.f. of 1.9 V and titrate with a soln. of  $\text{Na}_2\text{HPO}_4$ . Since the diffusion current  $i_d$  is proportional to the concn. of Mg, while the  $\text{Na}_2\text{HPO}_4$  is being added and Mg is being pptd. there is a corresponding decrease in  $i_d$ . When all the Mg is pptd., the further addition of  $\text{Na}_2\text{HPO}_4$  does not cause any further decrease in  $i_d$ . In determining  $5 \times 10^{-3}$  to  $6 \times 10^{-6}$  g of Mg the error is  $\pm 3.5\%$ . The method enables Mg to be determined with satisfactory accuracy at concn. up to  $2.5 \times 10^{-6}$  mg per ml, and may be used for the determination of Mg in food products.

C. D. KOPKIN

**50. The spectrographic determination of magnesium in bismuth-uranium alloys.** J. C. Cotterill (A.E.R.E., Woolwich Outstation, London). *A.E.R.E. Report C/R 2456*, 1958, 8 pp.—The alloy (1 g) is converted into oxide, 20 mg of which is ground with 200 mg of a spectrographic buffer (equal parts of ferric and ammonium sulphates) and the mixture is made into pellets (each weighing 9 to 12 mg). Three of these are then burned in succession in the d.c. arc, copper electrodes being used. The spectra are recorded on an Ilford Ordinary plate and the Seidel densities of Mg 2802.7, Fe 2778.8 and Fe 2797.8 Å are evaluated by non-recording micro-photometry, iron being used as internal standard. The method is valid for 50 to 700 p.p.m. of Mg; the coeff. of variation for single spectra is 5% at 300 p.p.m. W. J. BAKER

**51. Determination of hydrogen in magnesium by combustion.** M. Codell and G. Norwitz (Pitman-Dunn Lab., Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 1958, 18 (4), 265-269.—The metal sample (up to 15 g) is cleaned by scraping off its outer surface and stored in a desiccator before and after cleaning. It is placed in a large porcelain or alumina boat which is inserted in a sillimanite protective tube, and burnt in a stream of mixed O and A (250 and 100 ml per min., respectively), at 700° rising to 800°. The water formed by combustion of the hydrogen is absorbed in anhydrous and weighed. The blank is reduced to  $\pm 0.1$  mg by using all-glass apparatus, by heating the boats at 1100° and storing them in a muffle-furnace at 500°. The mixed inlet gases are purified by successive passage through a column of  $\text{CuO}$  at 800°, ascarite and anhydrous. No blank value was

obtained with porcelain boats, but they are attacked and can be used only once, whereas alumina boats can be used repeatedly after re-ignition. Argon controls the combustion of the sample, and prevents suck-back of gases into the apparatus. Carbon can be simultaneously determined by placing a tube containing  $\text{MnO}_2$  and anhydrous after the water-absorption tube, to remove oxides of S and N, and then absorbing the  $\text{CO}_2$  in ascarite and anhydrous. The detailed construction of the apparatus, its manipulation, and the handling of the sample are described. Results for 2 samples of Mg containing 0.002 and 0.007% of H show satisfactory replication.

R. E. ESSERY

**52. Determination of free magnesium oxide in magnesite and chromomagnesite refractories.** L. I. Gladysheva and S. M. Zubakov. *Trudy Inst. Stroil. i Stroi. Material., Akad. Nauk KazSSR*, 1958, 1, 160-169; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,415.—It is established that in the determination of free MgO in magnesite and chromomagnesite articles by boiling the sample in a 20% soln. of  $\text{NH}_4\text{Cl}$ , the results obtained are low by  $\approx 5\%$  because of partial dissolution of the MgO of forsterite, monticellite and spinels. A method is evolved for the determination of free MgO in magnesite, chromomagnesite and magnesiochromite refractories with a mixture of 80 ml of 25% aq.  $\text{NH}_3$ , 32 g of  $\text{NH}_4\text{Cl}$  and 120 ml of water as solvent. Treat 1 g of sample with the above mixture (100 ml) and boil for  $\approx 1.5$  hr., periodically adding hot aq.  $\text{NH}_3$  (1:2) to maintain the vol. of the soln. Filter off the insoluble residue, wash it 2 or 3 times with hot dil. aq.  $\text{NH}_3$  and again leach as above. Then wash the insoluble residue, ignite and weigh. Determine  $\text{SiO}_2$  in the filtrate by photometry of the molybdosilicate complex, total CaO and MgO by titration with EDTA (disodium salt), and CaO by complexometric titration after pptn. of  $\text{Mg}(\text{OH})_2$  with alkali; determine MgO by difference. The total amount of CaO and  $\text{SiO}_2$  passing into solution is  $\approx 0.5$  to 1.7%.

C. D. KOPKIN

**53. Determination of calcium in wolframite ore.** J. E. Mathers, G. V. Potter and N. W. Shearer (Sylvania Electric Products Inc., Towanda, Pa., U.S.A.). *Anal. Chem.*, 1958, 30 (8), 1412-1413.—Place the ore sample (1 g) in a fused silica boat and transfer to the tube of a combustion furnace maintained at 625° to 650°. Pass anhydrous HCl at  $\approx 30$  ml per min. for 30 min. Leach the residue from the cooled boat with HCl (1 + 1) (10 ml) and digest for 10 min. Filter into a 100-ml flask, wash with 10% HCl, add 50 ml of purified 2-butoxyethanol, dilute to the mark and mix. Calcium in the soln. is determined by flame photometry at a wavelength of 422.7 m $\mu$ . The method is said to be satisfactory for contents of Ca from 0.01% to 0.20%. It is claimed that a determination by this method can be carried out in 2 hr. Of the major elements in wolframite, all but a trace of Mn are removed by the HCl treatment. Titanium, Cr and Mo, originally present as minor impurities, are also absent after this treatment. F. L. SELFE

**54. Complexometric titration of calcium in the presence of magnesium.** A. D. Kenny and V. H. Cohn (Dept. of Pharmacol., Harvard Med. School, Boston, Mass., U.S.A.). *Anal. Chem.*, 1958, 30 (8), 1366-1368.—The determination of Ca in biological tissues by the EDTA titration method developed by Munson *et al.* (*cf. J. Dent. Res.*, 1955, 34, 714) is satisfactory provided that, in the

presence of Mg, the Mg to Ca ratio is 1 or less. It is now shown that interference due to Mg can be made negligible when this ratio is as high as 16 by controlling the pH of the final soln. at a value of 12.4 to 12.5. Experimental evidence is presented.

F. L. SELFE

**55. Simultaneous spectrophotometric micro-determination of calcium and magnesium with Eriochrome black T and ethylenediaminetetra-acetic acid.** V. P. Madhava Menon and M. Sankar Das (Chem. Div., Atomic Energy Estab., Trombay, Bombay, India). *Analyst*, 1958, **83**, 434-437.—From a comparison of the reduction of extinction of an Eriochrome black T soln. when an unknown soln. containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is added, with that caused when a soln. of Mg-EDTA is also added, the concn. of Ca and Mg can be calculated. Cations forming more stable complexes than does Mg must be removed or suppressed. The error of the method is  $\pm 10\%$  of the individual determinations when the concn. of either element in terms of Mg is 8 to 36  $\mu\text{g}$  per ml.

A. O. JONES

**56. Separation of alkaline-earth elements. IV. Co-precipitation of barium in the induced precipitate of lead sulphate.** Mutsuaki Shinagawa and Toshifumi Murata (Dept. of Chem., Fac. of Sci., Hiroshima Univ.). *Bull. Chem. Soc. Japan*, 1958, **31** (2), 162-165 (in English).—Barium ions induce the pptn. of  $\text{PbSO}_4$  and are themselves co-pptd. Barium concn. were measured by use of  $^{137}\text{Ba}$  as tracer and the  $\text{PbSO}_4$  was determined amperometrically. The various factors influencing the character of the ppt., such as ageing time and  $\text{H}_2\text{SO}_4$  concn., were studied. The conclusions drawn were that the amount of co-pptg. Ba follows the Freundlich adsorption isotherm, and is not proportional to the amount of  $\text{PbSO}_4$  pptg. The presence of ammonium acetate in the soln. before pptn. is responsible for the co-pptn. of a large proportion (85 to 99%) of the Ba present.

**V. Co-precipitation of radium in the induced precipitate of lead sulphate.** Mutsuaki Shinagawa and Toshifumi Murata. *Ibid.*, 1958, **31** (2), 166-168 (in English).—As in Part IV, Ba is used to induce the pptn. of  $\text{PbSO}_4$ , but also acts as a carrier for Ra. Various factors affecting the pptn. are discussed, and it is concluded that whether or not the pptn. was induced by Ba an approx. constant proportion of the Ra present (92 to 97%) was carried down, irrespective of the amount of  $\text{PbSO}_4$  pptd. The addition of ammonium acetate to the soln. before pptn. was necessary to secure the recovery of the high proportion of Ra.

G. S. ROBERTS

**57. Quantitative spectrochemical determination of barium and strontium.** R. J. Grabowski and R. C. Unice (Shell Development Co., Houston, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1374-1379.—The method is applicable to any sample that can be dissolved in HCl after fusion in a  $\text{Na}_2\text{CO}_3$  flux. The prepared sample soln. containing indium oxide as internal standard is excited by a high-voltage spark, with a rotating disc electrode. The coefficient of variation is  $<5\%$  for samples containing as little as 0.005% of Ba or Sr.

K. A. PROCTOR

**58. Rapid method for the determination of zinc in polymetallic ores and industrial by-products.** E. P. Ozhigov and A. N. Dorokhina. *Sobshch. o Nauch.-Issled. Rabot. Chlenov Primorsk. Otd. Vses. Khim. Obshch. im. D. I. Mendeleev*, 1957, (3), 65-72;

*Ref. Zhur., Khim.*, 1958, Abstr. No. 53,419.—To determine Zn in ores and by-products containing  $<1\%$  of Mn, moisten 0.1 to 2 g of the ore with water, add 15 or 20 ml of conc. HCl, boil for 25 min., add 25 ml of hot water and precipitate  $\text{Fe}(\text{OH})_3$  from the resulting soln. by the addition of 20 to 30 ml of conc. aq.  $\text{NH}_3$  in the presence of 1 ml of  $\text{H}_2\text{O}_2$  soln. [or 5 ml of a 5% soln. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  or 10 ml of bromine water.] Boil for 3 min., filter off the ppt., wash it 7 or 8 times with hot 5%  $\text{NH}_4\text{Cl}$  soln., boil the filtrate for 10 min., dilute to 200 ml, neutralise to litmus with HCl, add 6 ml of conc. HCl, boil, add 5 or 10 ml of a hot 10% soln. of  $\text{Na}_2\text{S}_2\text{O}_8$  (to precipitate  $\text{Cu}_2\text{S}$ ), boil for 3 min., cool to  $80^\circ$  and titrate with a soln. of  $\text{K}_4\text{Fe}(\text{CN})_6$  in the presence of the pptd.  $\text{Cu}_2\text{S}$  and S, with  $(\text{NH}_4)_2\text{MoO}_4$  as indicator. With a manganese content in the ore of 1 to 6%, after dissolution of the sample add 50 ml of hot water and 6 ml of conc. HCl, neutralise to litmus with aq.  $\text{NH}_3$ , heat to b.p., add 10 or 15 ml of a 10% soln. of  $\text{Na}_2\text{S}_2\text{O}_8$ , boil for 30 min. to separate  $\text{MnO}(\text{OH})_2$ , completely, add 40 to 50 ml of aq.  $\text{NH}_3$ , boil, filter off the ppt., wash it 10 times with a 5% soln. of  $\text{NH}_4\text{Cl}$ , and precipitate  $\text{Cu}_2\text{S}$  in the filtrate and determine Zn as described above.

C. D. KOPKIN

**59. Determination of zinc oxide in zinc powder.** C. G. Taylor (Chem. Dept., Coll. of Technol., Suffolk St., Birmingham, England). *Analyst*, 1958, **83**, 425-429.—Comparison of the results obtained by a gravimetric determination of Zn in a sample of zinc powder with those obtained by determination of ZnO in the powder by the method of Osborn (*Analyst*, 1951, **76**, 114), in which the ZnO is extracted with ammonium acetate soln., shows that in the extraction method some metallic Zn is dissolved. In the apparatus described, the extraction and subsequent filtration are made with exclusion of air. The ammonium acetate soln. and the sample are placed in a Buchner flask fitted with a rubber bung carrying a glass tube terminating in a filter disc. The flask is evacuated until the liquid boils at room temp., and a stream of N is then passed through for 5 min. The inlet for N and the filter-tube exit are closed and the flask is shaken and set aside for the appropriate time. The liquid is then forced through the filter disc by pressure of N applied through the side tube, and Zn is determined in an aliquot by oxine pptn. Results show that with exclusion of air the proportion of Zn dissolved from the powder is reduced from, e.g., 6 to 8% to 4 to 4.3%. The constancy of the results shows that under the conditions described only ZnO is dissolved by the ammonium acetate soln.

A. O. JONES

**60. Radiometric titration of zinc and cadmium with potassium ferrocyanide.** I. M. Gibalo and V. M. Byr'ko (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1958, **24** (3), 281-283.—Titration of Zn is carried out by means of a soln. of  $\text{K}_4\text{Fe}(\text{CN})_6$  containing  $^{59}\text{Fe}$ . During the titration, portions of the soln. being titrated are removed and their activity is determined. The method is also suitable for determining Cd. When Cd and Zn are present together, the total Cd plus Zn is determined in one aliquot and Zn alone is determined in another aliquot after removal of Cd by means of 5:6-benzoquinoline.

G. S. SMITH

**61. Separation of zinc and copper with cyanoacetamide in the determination of zinc.** R. H. Maier (Dept. of Agric. Chem. and Soils, Univ. of Arizona,

Tucson, U.S.A.). *Anal. Chim. Acta*, 1958, **18** (4), 321-323.—Cyanacetamide is used as a masking agent for Cu in the colorimetric determination of Zn with zincon (2-carboxy-2'-hydroxy-5'-sulphoformazylbenzene). The soln. (containing up to 50  $\mu$ g of Zn in 10 ml) is treated in a Pyrex-glass beaker with 10 ml of Clark and Lubs buffer (pH 9.4) and the pH is checked and adjusted if necessary. Solid cyanacetamide (40 mg) is added, and, after being thoroughly mixed, the soln. is transferred to a 50-ml Pyrex-glass flask, and treated with 1 ml of zincon soln. (0.13 g dissolved in 2 ml of N NaOH and made up to 100 ml). The soln. is mixed, made up to 50 ml, mixed again, and the colour read at 620 m $\mu$ . Results are referred to a standard curve. All reagents, standards and dilutions should be made with de-ionised water. The colour is stable for 30 min. Up to 100  $\mu$ g of Cu is masked, but Fe and Mn interfere. Other interferences are as previously reported (*cf.* Rush and Yoe, *Anal. Abstr.*, 1954, **1**, 2932).

R. E. ESSERY

62. Significance of the pointage titration in the control of zinc phosphating baths. F. J. Armon (G. K. N. Group Res. Lab., Birmingham New Rd., Lanesfield, Wolverhampton, England). *Analyst*, 1958, **83**, 374-376.—In industrial operations, control of phosphating baths is obtained by the pointage titration, i.e., the titre of 0.1 N NaOH required to neutralise a 10-ml aliquot of the bath soln. to phenolphthalein. Data that help to explain the reactions occurring during the titration have been obtained. The X-ray diffraction pattern of the ppt. present at the end of the titration, as well as its analysis, suggest that it is zinc orthophosphate,  $\text{Zn}_3(\text{PO}_4)_2$ . The calculated pointage agreed with that found for a synthetic soln., but with liquid from a nitrate-accelerated bath the observed value indicated that some constituent in addition to the total phosphate was being measured. This was considered to be due to reaction between  $\text{Na}_2\text{HPO}_4$  and the excess of Zn present to form  $\text{Zn}_3(\text{PO}_4)_2$ . With the inclusion of this reaction, the calculated figure agreed more closely with the observed titre. The pointage titration for zinc phosphate baths (and probably for iron and manganese phosphate baths) is a measure of the total  $\text{PO}_4^{3-}$  only if other heavy-metal salts, e.g.,  $\text{Zn}(\text{NO}_3)_2$ , are absent.

A. O. JONES

63. Products of the reaction between thioacetamide and mercury(II) salts. J. F. Vozza (Univ. Wisconsin, Racine, U.S.A.). *J. Chem. Educ.*, 1958, **35** (3), 145-146.—Data presented show the effect of pH and type of acid on the nature of ppt. formed by the reaction between thioacetamide and mercuric salts. The coloured forms of HgS pptd. are various forms of cinnabar and these can be converted into red cinnabar by the action of hot KOH. The black ppt. of HgS from both thioacetamide and  $\text{H}_2\text{S}$  are the same.

O. M. WHITTON

64. Purity test for metallic mercury used in polarography. Y. Israel (Israel Mining Ind. Lab., Haifa). *Analyst*, 1958, **83**, 432-434.—In some polarographic determinations large currents yielded by certain blank tests were found to be related to impurities in the mercury and a simple polarographic and amperometric method of testing the purity of the mercury, based on this observation, is described. Polarographic determinations were made with a Tinsley pen-recording polarograph, type MK/14

and amperometric measurements with a home-made apparatus similar to that described by Kolthoff and Lingane ("Polarography," 2nd Ed., Interscience Publishers Inc., New York, 1952, pp. 299-301). For each determination 10 ml of one of the following base soln. was added to a 20-g sample of the mercury to be tested in the pool electrode, a specially purified mercury being used in the dropping electrode. The two base soln. used were (i), a soln. M in aq.  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  containing 0.01% of gelatin and 2% of  $\text{Na}_2\text{SO}_3$ , and (ii), a soln. M in NaOH containing 2% of  $\text{Na}_2\text{SO}_3$ . With purified mercury in the pool electrode no initial wave (or only a negligible one) appears from the zero current line. With impure mercury an initial sharp rise of a wave from the zero current line occurs.

A. O. JONES

65. Separation of mercury from other metals with ion-exchange resins. I. Ubalini and S. Cassata (Ind. Chem. Inst. of Polytech., Milan, Italy). *Ann. Chim., Roma*, 1958, **48** (3), 205-208.—Mercury may be separated from other cations by conversion into the complex anions  $\text{HgCl}_4^{2-}$  and  $\text{HgCl}_6^{4-}$  with HCl, followed by passage through the cation-exchange resin Amberlite IR-120. In the form of the complex anion, the Hg is not retained, whereas Fe, Ti, Cu, Zn, Cd, Ni, Co, Al, Sn, Ba, Mg and the alkali metals are retained. The procedure is illustrated by the separation and determination of Hg in  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ .

A. G. COOPER

66. Catalytic determination of mercury with potassium ferrocyanide and nitrosobenzene. J. Agterdenbos, E. R. Van Der Worm and R. W. Van Norren (Lab. for Anal. Chem., Univ. of Amsterdam, Holland). *Anal. Chim. Acta*, 1958, **18** (4), 380-383.—Mercury catalyses the formation of a violet complex between  $\text{K}_4\text{Fe}(\text{CN})_6$  and nitrosobenzene, and the original method of Asperger and Murati (*cf.* *Anal. Abstr.*, 1954, **1**, 1789) is modified by buffering the reaction at pH 3.9 to 4.1. To a mixture of 10 ml of nitrosobenzene soln. ( $4.2 \times 10^{-3} M$ ), 25 ml of buffer soln., and the soln. to be analysed, add water to a total vol. of 90 ml. Place in a thermostat at 25° and add 10 ml of  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. ( $0.005 M$ ) at the same time, and read the extinction in exactly 15 min. at 528 m $\mu$  against a blank similarly treated. The thermostat should be kept in semi-darkness, but since only light of <350 m $\mu$  influences the reaction, it may be possible to work in red or yellow light. Results for 0.5 to 7.0  $\mu$ g of Hg showed a coeff. of variation of  $\pm 5.0\%$  as compared with  $\pm 9.5\%$  for the original method. It may be possible to extend the range by using smaller volumes or longer reaction times. Gold and Pt have a weak catalytic effect, other elements have a negative salt effect, and the catalytic effect of some mercury compounds does not follow that of  $\text{HgCl}_2$  (*cf.* Asperger and Parlovic, *J. Chem. Soc.*, 1955, 1449).

R. E. ESSERY

67. Determination of boron in boron hydrides and derivatives by the carmine method. W. H. Hill, J. M. Merrill and B. J. Palm (Univ. Pittsburgh, Pa.). *U.S. Atomic Energy Comm., Rep. CCC-1024-TR-223*, 1957, 10 pp.—The carmine method for the determination of 1 to 10  $\mu$ g of B was applied to dimethylaminoborane, trimethylaminoborane, pyridineborane and decaborane. The colour produced on addition of carmine in conc.  $\text{H}_2\text{SO}_4$  is measured with a spectrophotometer. The non-specific method does not differentiate between B in boron hydrides and in  $\text{B}(\text{OH})_3$  or  $\text{B}_2\text{O}_3$ .

NUCL. SCI. ABSTR.

68. **Determination of traces of boron in nickel.** C. L. Luke (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1405-1406.—Decompose the sample (0.1 g) with HCl-platinic chloride soln. (1 ml) [2.5 ml of platinic chloride soln. (1%) with 500 ml of HCl (1 + 1)] by heating in a 100-ml flask under a reflux condenser. Add methanol and adjust the pH until the soln. is just acid to methyl orange. Distil methyl borate, and determine boron by the photometric curcumin method. Carry a reagent blank through the whole analysis. The accuracy of the method was checked by using a 0.03% boron-nickel alloy; results for several determinations on proprietary alloys are reported. It is claimed that the method can be used to determine acid-soluble boron in metals or materials soluble in HCl.

F. L. SELFE

69. **Photometric determination of traces of boron in silicon after separation by a hydrothermal refining technique.** C. L. Luke and S. S. Flaschen (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1406-1409.—Silicon (1 g) is converted into crystalline quartz by heating with 0.5% NaOH soln. (14 ml) in a platinum-lined autoclave (capacity 21 ml) for 5 hr. at 350° and about 5000 p.s.i. Boron, as borate, plus a little silicate, remains dissolved in the mother liquor, and is isolated by a methanol distillation before determination by the photometric curcumin method. This method of separation makes it possible to analyse 1-g samples of silicon with no increase in the reagent blank. The limit of sensitivity of the photometric method can thus be extended to 0.02 p.p.m. without loss of accuracy. Tests on synthetic sample mixtures show that boron is quantitatively separated from silicon by this method.

F. L. SELFE

70. **Spectrophotometric determination of boron in aluminium alloys of high silicon content with 1:1'-dianthrimide.** G. Matelli (Ist. Sper. dei Metalli Leggeri, Novara, Italy). *Aluminio*, 1957, **26**, 255-257.—The photometric determination of B with 1:1'-dianthrimide described by Brewster (*Anal. Chem.*, 1951, **23**, 1809) is applied to aluminium alloys containing  $\approx 4$  to 6% of Si. The insol. residue from treatment of the sample with acid can be filtered off and rejected, as the amount of B present is less than the analytical error. *Procedure*.—The sample (0.1 g) is dissolved in 5 ml of acid mixture (200 ml of  $H_2SO_4$ , 300 ml of HCl, 300 ml of  $HNO_3$  and 750 ml of  $H_2O$ ) in the presence of 5 ml of a satd. CaO soln., and the soln. after filtration is diluted to 100 ml. A 5-ml aliquot is evaporated to fumes with 6 ml of  $H_2SO_4$ , and 12.5 ml of 1:1'-dianthrimide reagent (0.1 g in 25 ml of conc.  $H_2SO_4$ , 5 ml of which is diluted to 200 ml with conc.  $H_2SO_4$  just before use) is added. The soln. is maintained at precisely 90° in an oven for 4 hr., and is then diluted to 25 ml with conc.  $H_2SO_4$ . The extinction of the soln. is measured relative to that of a blank at 620 m $\mu$ .

J. H. WATON

71. **Analyses by the use of fluorotitanic acid and hydrogen peroxide. III. Determination of boric acid.** Hisao Fukamauchi, Miko Sekiguchi and Kazuko Doguchi (Women's Dept., Tokyo College of Pharm., Ueno-sakuragicho, Taito-ku). *Japan Analyst*, 1958, **7** (3), 166-169.—The yellow colour of pertitanate (cf. *Anal. Abstr.*, 1958, **5**, 425) is produced when  $H_2BO_3$  is added to a soln. containing

fluorotitanate and  $H_2O_2$ ; the extinction is proportional to the amount of  $H_2BO_3$  (2 to 18 mg per 25 ml) in  $N H_2SO_4$ . The sample is made up to 25 ml after the addition of 10  $N H_2SO_4$  (2 ml) and 5 ml of the reagent (2.08 g of  $Na_2TiF_6$ , 1.68 g of NaF, 1.1 ml of 30%  $H_2O_2$  and  $H_2SO_4$  made up to 100 ml to give a  $N H_2SO_4$  soln.).

K. SAITO

72. **New method for the determination of boric acid by the formation of a complex with calcium gluconate.** C. Liteanu and E. Motiu (Inst. of Chem., Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1957, **8** (3-4), 243-250.—It is claimed that the determination of boric acid ( $>2$  mg) as a complex with calcium gluconate by titration with NaOH, with phenolphthalein as indicator, or by conductimetric or potentiometric titration, gives results as good as those obtained by the mannitol method. It is also claimed that the titration of boric acid by neutralisation can be achieved by complexing with a salt of an organic hydroxy acid, provided that this acid has two hydroxyl groups in the *cis*-position, apart from the hydroxyl group next to the carboxyl group. Evidence of a new borodigluconate complex is given.

H. SHER

73. **New reagent for the colorimetric determination of aluminium.** H. Green. *Metallurgia, Manchr.*, 1958, **57**, 157-158.—When a mixture of aluminon and ferron is used as reagent, a wider range of aluminium contents can be determined than with aluminon alone. No colloidal stabiliser is required and the calibration graph is linear. A 1-g sample (e.g., cupola slag) is dissolved in 20 ml of  $HClO_4$  (sp. gr. 1.54), diluted, electrolysed in a mercury-cathode cell at 3 amp. for 1 hr., and the electrolyte is made up to 200 ml. To a 5-ml aliquot are added 3 ml of HCl (25%) and 3 ml of aq. cupferron (6%) to precipitate Fe and Ti, which are extracted with  $CHCl_3$ . An aliquot of the remaining liquid is taken and  $HClO_4$  and  $HNO_3$  are added; after evaporation, HCl is added, the solution is diluted, and ferron and aluminon reagents are added, together with an acetate buffer. The solution is warmed, then cooled, and the absorption is measured at 520 m $\mu$  against a blank.

S.C.I. ABSTR.

74. **Iodimetric determination of aluminium via the basic arsenate.** G. B. Shakhhtakhtinskii and I. A. Mamedov. *Trudy Azerb. Ind. Inst.*, 1957, (10), 273-279; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,028.—The method evolved is based on pptn. of Al as  $Al_3(OH)_3(AsO_4)_3$  solution of the resulting ppt. in  $H_2SO_4$  and iodimetric titration of the arsenic acid liberated. To 10 ml of the soln. to be analysed add  $NH_4Cl$  (1 to 1.5 g), aq.  $NH_3$  (to a faint cloudiness), conc. HCl (to dissolve the cloudiness, 1 or 2 drops), 50% acetic acid (3 ml) and 2N ammonium acetate (2 ml), and heat to boiling. Dilute 6 to 10 ml of 0.5  $N Na_2HASO_4$  to  $\approx 15$  ml, heat to boiling and add to the boiling analytical soln. After 3 or 5 min. filter off the ppt., wash it 6 or 7 times with a hot 2% soln. of  $NH_4Cl$ , then dissolve it in dil.  $H_2SO_4$  (1:2.5). To the resulting soln. add 20 or 25 ml of benzene or  $CHCl_3$  and 3 ml of 2  $N KI$ , mix, dilute with an equal vol. of water and titrate with 0.01 or 0.1  $N Na_2S_2O_3$  till the organic layer is colourless. The determination takes 30 to 40 min. The error is  $>0.017$  mg of Al.

C. D. KOPKIN

75. **Determination of aluminium after isolation with sodium hydroxide and sodium chloride.** Tsui-Lin Chien (Inst. of Mineral Materials, Min. of



Geology). *Acta Chim. Sinica*, 1957, **23** (5), 324-329 (from English summary).—Aluminium is separated from Fe and Ti by excess of NaOH and NaCl, then titrated with EDTA. The amounts of Al, Fe and Ti can vary through a considerable range and the method is applicable to ores and silicate rocks. In order to obtain consistent results a modification has been introduced into the titration using haematoxylin as indicator; this gives a sharp end-point. S.C.I. ABSTR.

**76. Spectrographic analysis of alumina and hydrated aluminium oxide.** L. V. Drutskaia. *Trudy Vses. Nauch. Alumin.-Magn. Inst.*, 1957, (40), 230-253; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,395.—Place the samples and standards in a cavity in a carbon electrode of diam. 3 mm and depth 3-5 mm. Excite the spectra in a condensed spark at 3 amp. with capacity 0.01  $\mu$ F and self induction 0.15 mH with the secondary gap 2-8 mm and the analytical 3 mm. The sparking lasts 12 sec. Photograph the spectra on a medium spectrograph with slit width 0.04 mm and exposure 40 sec. Carry out parallel analyses by exciting the spectra in an a.c. arc at 5 amp. To increase the reproducibility of the analytical results, interrupt the exposure every 5 sec. and add fresh portions of material to the cavity. The analysis was carried out in the concn. ranges— $\text{Fe}_2\text{O}_3$  0.01 to 0.2;  $\text{Na}_2\text{O}$  0.1 to 3.0;  $\text{SiO}_2$  0.01 to 0.5; and  $\text{CaO}$  0.005 to 0.1%, by the lines Fe 2599-396, Na 3302-3, Si 2506-8 and Ca 3179-3 Å. The comparison lines were Al 3050-0 and 2669-1 Å. In the analysis in the arc discharge the lines used were Fe 3020-64 and Al 2652-4 and 2459-8 Å. The standards and samples must have similar compositions. C. D. KOPKIN

**77. New fluorescent indicators. II. Volumetric determination of aluminium and zinc.** Z. Holzbacher (Inst. Anal. Chem., High-School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (3), 430-438.—The yellow-green fluorescence of  $\text{Al}^{3+}$  with *o*-salicylideneaminophenol (I) and the blue fluorescence of  $\text{Zn}^{2+}$  with the acetylhydrazine of salicylaldehyde (II) disappear on the addition of fluorides (with Al) or of EDTA (disodium salt) (III) (with Zn). This can be used for the fluorimetric determination of Al and Zn in the presence of other metals. *Procedure for Al*—To 10 ml of the slightly acid soln. (pH 4 to 5) containing 20 to 40 mg of Al add acetate buffer soln. (10 ml) and I (0.05% in ethanol) (2 ml) and titrate in u.v. light with NaF soln. till the fluorescence disappears (1 drop in 3 to 5 sec.). Compare with a blank. The relative error is  $\pm 1\%$ . There is no interference from Na, K, Li,  $\text{NH}_4^+$ , Ti, Ag, Cd, Ni, Co, Zn or Mn in excess, nor from 10 to 35 mg of Pb, Hg, As, P, U, Cr, Mg, Ca, Ba, Sr, Ti, Ce, Th, Zr, La, Be, Sb or Sn; coloured ions (mainly  $\text{Fe}^{3+}$ ) and tartrates interfere. Small amounts of Bi and Cu can be masked with thiosulphate. *Procedure for Zn*—To 10 or 20 ml of a neutral soln. containing 4 to 170 mg of Zn add acetate buffer soln. (10 ml) and II (0.1% in ethanol) (2 ml) and titrate slowly with stirring with III till the fluorescence disappears. An excess of Na, K, Li,  $\text{NH}_4^+$ , Ti, Ag, Sr, Ba, F<sup>-</sup>, tartrates and thio-sulphates, and small amounts of  $\text{AsO}_4^{3-}$ ,  $\text{AsO}_3^{3-}$  and phosphates do not interfere. Interference by Hg, Cu, Cd, Bi, Pb, Mo, Ti, Zr, Be, Ce, Th, La, Al, Ni, Co, Mn,  $\text{Fe}^{3+}$ , Cr and U (in excess) has been observed, but can be avoided by addition of thio-sulphate (for Hg and Cu) or of fluoride (for Al, La, Fe, Ti, Zr, Be, Th and  $\text{Ce}^{4+}$ ). The relative error is -0.16 to +0.45%. J. ŽYKA

**78. Determination of aluminium, nickel, cobalt, copper and iron in Alnico.** D. H. Wilkins and L. E. Hibbs (Res. Lab., Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (4), 372-375.—The sample (1 g) is dissolved in aqua regia, and  $\text{HNO}_3$  is removed by double evaporation. To the resulting syrup are added 50 ml of water and 5 ml of conc. HCl, and Cu is separated by electrolysis at 0.5 amp. with a divided cell. The Cu is stripped from the electrode by reverse electrolysis into 10 ml of 20% aq. Na acetate soln., excess of 0.01 M EDTA is added and back-titrated with a standard copper soln., with 1-(2-pyridylazo)-2-naphthol as indicator. The Cu-free soln. is treated with 3 ml of 30%  $\text{H}_2\text{O}_2$  and evaporated to 4 to 5 ml, and transferred to a column (35 cm  $\times$  1 cm) of Dowex 1-X4 (100 to 150 mesh, chloride form), which has been previously washed with 9 M HCl. The Al and Ni are eluted with 2 column-volumes of 9 M HCl, then the eluent is changed to 4 M HCl, and when the blue cobalt band is within 5 cm of the bottom of the column the receiver is changed to collect the cobalt eluate. Finally, the Fe is eluted with 0.5 M HCl. Each of the three eluates is evaporated to 10 ml, made up to 250 ml with water, and 25-ml aliquots are mixed with 10 ml of buffer (pH 4.8). Aluminium and nickel together are determined in one aliquot by adding a small excess of EDTA and back-titrating at boiling-point with standard copper soln. Aluminium is then determined by adding 1 g of  $\text{NH}_4\text{F}$  to the hot mixture, and titrating the EDTA liberated from its complex with standard copper soln. Iron and cobalt are determined in the other aliquots by adding a 5 to 10-ml excess of EDTA and back-titrating with standard copper soln. to appropriate end-points. Results for two Alnico samples showed good reproducibility and satisfactory agreement with results by classical wet methods. R. E. ESSERY

**79. Spectrophotometric determination of a small amount of aluminium in tin and lead alloys.** Kazuo Ota (Toyota Motor Co., Koromo, Aichi-ken). *Japan Analyst.*, 1958, **7** (3), 162-166.—For the determination of Al (<0.1%) by the aluminum (I) method, Sn is volatilised with HBr and  $\text{H}_2\text{SO}_4$  (cf. Ota and Mori, *Anal. Abstr.*, 1957, **4**, 1486). Pb is pptd. as  $\text{PbSO}_4$ , and other interfering metals are removed by mercury-cathode electrolysis. The amount of  $\text{SO}_4^{2-}$  affects the colorimetry and must be kept constant. *Procedure*—Decompose the sample (1 g) with  $\text{H}_2\text{SO}_4$  (20 ml) and heat with HBr (sp. gr. 1.48) (15 ml) to between 200° and 220°. Evaporate the residue to 5 ml, dissolve it in water (100 ml) and electrolyse (10 amp.) until the soln. gives a negative test with  $\text{Na}_2\text{S}$  paper. Evaporate the soln. to 3 ml, add  $\text{H}_2\text{SO}_4$  (7 ml) and water, neutralise with aq.  $\text{NH}_3$  soln. (to *p*-nitrophenol), add 5 N HCl (4 ml) and dilute to 100 ml. Make up a 25-ml portion to 100 ml after the addition of ammonium buffer (156 g of ammonium acetate and 108 g of  $\text{NH}_4\text{Cl}$  per litre) (5 ml), thioglycolic acid (10%, 1.5 ml), I (0.2%, 2 ml) and acacia gum soln. (5%, 2 ml), and heat in a boiling-water bath for 10 min. Measure the extinction at 535 m $\mu$ . K. SAITO

**80. Volumetric vanadatometric determination of gallium.** S. Ya. Vinkovetskaya and V. A. Nazarenko. *Zavod. Lab.*, 1958, **24** (3), 268-270.—The method is based on the use of 5:7-dibromo-8-hydroxyquinoline (I) (cf. Nazarenko and Vinkovetskaya, *Anal. Abstr.*, 1957, **4**, 2264) which



precipitates Ga without interference from large amounts of Al, Ti (in the presence of  $H_2O_2$ ), In, Pb, Cd and Mn and from small amounts of Sb and W. Preliminary separation of Ga is necessary in the presence of Fe, Cu, Zn and Sn. Separation of Ga can be carried out either by precipitating it together with Al as collector by means of pyridine, or by extraction of  $GaCl_3$  with ether. With the former method, the soln. of the sample (an alloy based on Al, Fe, Cu or other metal) in HCl is twice evaporated to dryness with HBr - Br mixture, and the residue, moistened with HCl, is dissolved in 150 ml of water. Aq.  $NH_3$  and HCl are added to make the soln. slightly acid and it is then treated with 3 ml of dil. HCl (1:1), 5 g of hydroxyammonium chloride and 3 g of  $NH_4Cl$  followed, after heating, by 25 ml of 20% pyridine soln. The hot soln. is filtered after 30 min. If large amounts of Cu and Zn are present the pptn. is repeated. If Al is absent, 50 mg in the form of  $NO_3^-$ ,  $SO_4^{2-}$  or  $Cl^-$  is added before the pptn. The ppt. is washed with a 3% soln. of  $NH_4NO_3$  containing 1% of hydroxyammonium chloride and 3 drops of pyridine, and dissolved in hot dil. HCl (1:1) (4 ml). The filter is washed with hot water (100 ml) and the Ga in the filtrate after treatment with 0.5 ml of 30%  $H_2O_2$  soln. and 20 ml of acetone is pptd. by I. With the extraction method, metallic Cd is placed in the sample soln. (3 N in HCl) to reduce  $Fe^{2+}$  and precipitate heavy metals. The colourless filtered soln. is treated with 0.2 ml of a 20% soln. of  $TiCl_3$  in dil. HCl (1:1) and then made 6 N in HCl. The soln. is extracted with ether (3 × 15 ml), the combined extracts are washed with 6 N HCl (2 × 3 ml) and the Ga is re-extracted with water (3 × 15 ml). The aq. extracts are washed with ether, dissolved ether is removed by heating, the soln. is diluted to 100 ml, 20 ml of acetone and 4 ml of dil. HCl (1:1) are added and Ga is pptd. by I. The method gave satisfactory results with alloys containing 0.5 to 5% of Ga.

G. S. SMITH

**81. Polarographic determination of indium in zinc-base alloys. I. General introduction. Application of the linear-sweep cathode-ray polarograph.** G. F. Reynolds and H. I. Shalovsky (Min. of Supply, Chem. Inspectorate, Royal Arsenal, Woolwich, England). *Anal. Chim. Acta*, 1958, **18** (4), 345-349. —The major problem in the polarographic determination of In is the coincident reduction of Cd. By using the derivative circuit of the linear-sweep cathode-ray polarograph (cf. Reynolds and Davis, *Analyst*, 1953, **78**, 314) these waves can be separated if the disparity in concn. is not too great. Boil the alloy (10 g) in 45 ml of 10 M HCl, and add 100-ml.  $H_2O_2$  till dissolution is complete. Evaporate to 15 ml, transfer to a 25-ml flask, make up to vol., transfer a 3-ml aliquot to the polarograph cell, and de-oxygenate by bubbling H or N for 10 min. Set the start potential of the polarograph at -3.0 V, and, with the instrument set for derivative working at a sensitivity setting  $S_1$ , measure the height  $h_1$  of the peak due to In at -0.56 V vs. the mercury-pool anode. Add 0.1 ml of a standard soln. of In (0.010 g in 250 ml of  $H_2O$  containing 5 ml of 10 M HCl), stir with the gas stream for 30 sec., then measure the height of the peak due to In,  $h_2$ , and note the sensitivity setting  $S_2$ . The  $In(p.p.m.) = 10S_2h_1/(3.1S_1h_2 - 3.0S_2h_1)$ . Concn. of In of 1.0 p.p.m. or more can be measured if the Cd to In ratio is  $>10$ , otherwise In can be reported as less than one-tenth of the determined content of Cd. The method can be modified for the determination of Cu, Pb and Cd.

R. E. ESSERY

**82. Properties of indium hydroxide and the separation of indium from zinc.** E. N. Deichman (N.S. Kurnakov Inst. of Gen. and Inorg. Chem., Acad. Sci., USSR). *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 1958, (3), 257-265.—The solubility of  $In(OH)_3$  in dil. NaOH soln. is negligible and even in 4 M to 8 M NaOH does not exceed  $2 \times 10^{-3}$  M. There is no evidence of the presence of stable soluble or insoluble indates. In 0.05 M NaOH,  $In^{3+}$  and  $Zn^{2+}$  are quant. pptd. When NaOH is added Zn begins to pass into soln. and with 3 M NaOH it is completely in soln. and separated from In. In the presence of  $Na_2CO_3$ , some Zn remains in the ppt. when the NaOH concn. has attained 5 M.

G. S. SMITH

**83. Polarographic determination of impurities in purest indium.** F. A. Pohl and W. Bonsels (AEG-Forschungsinstit., Belecke/Möhne). *Z. anal. Chem.*, 1958, **161** (2), 108-114.—Impurities are concentrated by extraction with diisopropyl ether. Two separate 5-g samples are dissolved in 5 N HBr and the soln. are extracted with diisopropyl ether (300 ml) for 6 hr. The acid layer from each sample is evaporated to dryness with  $HClO_4$ , which is fumed off. The residue of one sample is evaporated with  $H_2SO_4$  and then dissolved in  $>1$  ml of 0.5 M sodium tartrate (pH 4.5) and Cu, Bi and Pb are determined polarographically. In the amounts expected the sulphates dissolve completely. The residue from the second sample is dissolved in  $>1$  ml of 6 N aq.  $NH_3$  and Cu, Cd and Zn are determined polarographically. A third 5-g sample is dissolved in HCl, diluted to 6 N in HCl and 1 drop of  $H_2O_2$  is added. The soln. is shaken for 3 min. with diisopropyl ether (3 × 20 ml), and the ether phase is back-extracted with 6 N HCl. After the addition of 1 drop of hydrazine sulphate soln., the ether soln. is evaporated to dryness. The residue is treated with  $HClO_4$ , which is fumed off, and then with  $H_2SO_4$  and hydrazine sulphate and evaporated. To the residue are added 1 drop of freshly prepared metol soln. and 1 ml of 0.5 M ammoniacal ammonium tartrate, and Ti and Fe are determined polarographically in the soln. These impurities can be determined within  $\pm 10\%$  in concn. down to  $10^{-4}\%$ .

G. BURGER

**84. Determination of metal ions with hexamminocobaltic chloride and sodium fluoride. I. Gravimetric determination of scandium.** Yoshimasa Takashima (Fac. of Sci., Kyushu Univ., Hakozaki, Fukuoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (3), 243-246.—Beck's microscopical detection of Sc with  $[Co(NH_6)_6]Cl_3$  (I) and NaF (*Mikrochim. Acta*, 1949, **34**, 423) was applied to the gravimetric determination. The pptn. (0.5 to 5 mg of Sc) proceeds quant. at pH 3 to 4 (in a polyethylene beaker) in the presence of 2 to 5 ml of 0.05 M I and  $\approx 2$  ml of 3% NaF in 25 ml. The ppt. is filtered off after 2 hr., washed with water (3 × 20 ml), dried at  $110^\circ$ , and weighed as  $[Co(NH_6)_6]ScF_6$ . There is interference from Fe, Al and Si; fluorides of Th, Bi and rare earths are filtered off before the addition of I. In the presence of Cd, Ti, Be and Zr, the amount of F<sup>-</sup> must be increased.

**II. Radiometric analysis of scandium.** Yoshimasa Takashima. *Ibid.*, 1958, **79** (3), 246-248.—With the aid of I containing  $^{59}Co$ , the gravimetric determination can be extended to 5 to 300  $\mu g$  of Sc. The ppt. obtained similarly is, after being washed, dissolved in HCl (1 + 1, 3 ml) and evaporated in a glass dish; the radioactivity is measured with an electroscope. The error is  $<10\%$  for  $>5 \mu g$  of Sc.

K. SAITO

85. Spectrographic method for the quantitative determination of scandium in natural materials and coal ash. O. A. Kul'skaya and O. F. Vdovenko. *Ukr. Khim. Zhur.*, 1957, **23** (6), 799-804; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,032.—Excite the spectra in a d.c. arc discharge at 10 amp. and photograph them on a large Hilger spectrograph. In direct analysis use as base for standards a rock, mineral or ash which does not contain Sc. To concentrate the Sc, precipitate it with Th, Zr, La or a rare earth. In this case prepare the standards on a base of  $\text{ThO}_2$  or a mixture of rare-earth oxides. Use Zr as internal standard; mix powdered carbon containing 2% of Zr with the samples and standards in the ratio 1:2. Construct a calibration curve on the co-ordinates  $\Delta S$  and  $\log C$  from the lines (in Å)—Sc 2552.3 and Zr 2550.7, and Sc 3353.7 and Zr 3357.2; in the analysis of zircon the line at 3353.7 Å is not suitable. The error of the analysis is up to 13% for concn. of Sc from 0.002 to 0.2%.

C. D. KOPKIN

86. Separation of scandium from sedimentary rocks, coal ash and certain minerals prior to its determination. G. Ya. Gorn'yi. *Ukr. Khim. Zhur.*, 1957, **23** (6), 792-798; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,031.—The conditions are studied for the separation of small amounts (0.001 to 0.02%) of Sc from a large number of sedimentary rocks containing 0.1 to 0.5% of the rare-earth elements, but not containing Th. It is established that the normal methods for the separation of small quantities of Sc together with the rare earths as oxalates or fluorides in the presence of large amounts of other elements (Al, Ti) do not lead to complete separation of Sc. The co-pptn. of Sc with the rare earths as oxalate becomes quant. if Al is first removed with excess of NaOH. Dissolve the oxalate ppt. in dil. HCl or  $\text{HNO}_3$  (1:1) and precipitate Sc by the addition of a 10% soln. of phytin. Very small amounts of Sc which are not pptd. by this procedure and traces of Sc remaining in the oxalate filtrate may be co-pptd. with Th. Fuse the ignited phytates of Sc and Th with NaOH, dissolve the melt in dil.  $\text{HNO}_3$  (which takes up all the Sc and part of the Th), filter and precipitate the hydroxides with aq.  $\text{NH}_3$ . Dissolve the ppt. in  $\text{HNO}_3$  (1:3) and precipitate Th with  $\text{KIO}_3$ . Re-precipitate the hydroxides from the filtrate, dissolve them in  $\text{HNO}_3$  (1:4) and repeat the pptn. with phytin from a small vol. ( $\approx 25$  ml); a further ppt. of pure Sc phytate is thus obtained. The oxalate-phytate method may be used for the determination of Sc in minerals and rocks which do not contain large amounts of Ti. To determine Sc in coal ash and Ti-containing rocks, use co-pptn. with Ti, and for the determination of Sc in zircon use co-pptn. with Zr. In the absence of large quantities of Al the phytate method of co-pptn. of Sc with Th (or Ti or Zr) does not necessitate preliminary removal of Al.

C. D. KOPKIN

87. Spectrographic analysis of small samples of actinium. N. I. Kalitchevskii and A. N. Razumovskii (A. A. Zhdanov State Univ., Leningrad). *Atomnaya Energiya*, 1957, **3** (12), 548-550; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,359.—In the spectrographic analysis of preparations of Ac, which possess strong  $\alpha$ - and  $\beta$ -activity and weak  $\gamma$ -activity, it is necessary that that part of the apparatus where the excitation of the spectra takes place be hermetically sealed; the use of chambers of lead glass or lead blocks is unnecessary. Excite the spectra in a glass tube with side arms closed with quartz windows. Pass a stream of  $\text{CO}_2$  through the tube.

Place the tube in a hermetically sealed plexi-glass chamber. Before changing the electrodes fresh portions of  $\text{CO}_2$  are passed through the tube. Excite the spectra between carbon and copper electrodes using a condensed spark and a.c. arc discharge and introducing the soln. on to the flattened end of the electrode. Steep the ends of the carbon electrodes in a polystyrene soln., and introduce Na into the samples to stabilise the discharge. Determine Na in the samples using a condensed spark discharge between copper electrodes. Photograph the spectra simultaneously on three spectrographs—on a large one with glass optical system, on a medium one in the u.v. region, and on a glass spectrograph with  $F = 270$  mm. The wavelengths of 54 Ac lines in the u.v. region are determined. It is established that, in comparison with the other actinides, Ac has a spectrum poor in lines. Several photographs of the spectra of samples containing 15 to 30  $\mu\text{g}$  of Ac were taken; a series of impurities was thereby observed.

C. D. KOPKIN

88. Ion-exchange chromatographic separation of radio-isotopes of the rare-earth elements. A. K. Lavrukhina, F. I. Pavlotskaya, A. A. Pozdnyakov and I. M. Grechishcheva. *Zhur. Neorg. Khim.*, 1958, **3** (1), 82-87; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,424.—The influence of the amount of the elements on the shape and position of the peaks on the elution curve in the chromatographic ion-exchange separation is shown. It is established that on decreasing the amount of the elements there is in a number of cases an increase in the rate of their elution. This is explained by a displacement in the equilibrium which is established in the eluent in favour of the complex forms. With a very small concn. of the elements the elution is characterised by narrow peaks. The observed displacement of the peaks may lead to a lower degree of separation by the chromatographic ion-exchange method.

C. D. KOPKIN

89. Manometric estimation of the carbon dioxide content of gas mixtures. H. Graetz and E. Negelein (Inst. f. Med. u. Biol., Dtsch. Akad. der Wissenschaften, Berlin). *Biochem. Z.*, 1958, **329** (6), 463-466.—The theoretical basis for the determination of  $\text{CO}_2$  by its reaction with  $\text{HPO}_4^{3-}$  and  $\text{H}_2\text{O}$ , forming  $\text{H}_2\text{PO}_4^-$  and  $\text{HCO}_3^-$ , and subsequent manometric determination of the  $\text{HCO}_3^-$  by its reaction with  $\text{H}_2\text{SO}_4$  is discussed. Some results of such determinations are reported.

G. W. CAMBRIDGE

90. Potentiometric analysis with glass electrodes of mixtures of weak acids [carbon dioxide and hydrogen sulphide]. M. A. Vorsina. *Sb. Nauch. Rabot. Moskov. Inst. Nar. Kh.*, 1957, (10), 343-352; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,422.—A method is evolved for the determination of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , when present together, by differential titration with NaOH soln. with two glass electrodes. In the differential titration of  $\text{CO}_2$  the titration curve shows two maxima; the first corresponds to the neutralisation of the first  $\text{H}^+$  of  $\text{H}_2\text{CO}_3$  (transition to  $\text{HCO}_3^-$ ) and the second to full neutralisation of the  $\text{H}_2\text{CO}_3$ . On the titration curve of a soln. containing  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , the first max. corresponds to the neutralisation of the first  $\text{H}^+$  of the  $\text{H}_2\text{CO}_3$  and the second to the neutralisation of the first  $\text{H}^+$  of the  $\text{H}_2\text{S}$ . The max. corresponding to complete neutralisation of the  $\text{H}_2\text{CO}_3$  is less distinct. The point on the curve corresponding to complete neutralisation of the  $\text{H}_2\text{S}$  could not be reliably

established. In the differential titration of 1.36 to 2.085 ml of 0.1 N  $H_2CO_3$  and 1.46 to 12.874 ml of 0.1 N  $H_2S$  in a total volume of 50 ml with 0.1035 N NaOH, the error of the determination is 0.34 to 0.53% and 0.153 to 0.35%, respectively.

C. D. KOPKIN

**91. Colorimetric determination of cyanide. Tris-(1:10-phenanthroline) - iron(II) ion as a selective and sensitive reagent.** A. A. Schilt (Dept. of Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1409-1411.—Up to 200  $\mu$ g of  $CN^-$  can be determined by the formation, and extraction into  $CHCl_3$ , of the neutral dicyanobis-(1:10-phenanthroline) -  $Fe^{II}$  complex, prepared by the reaction between tris-(1:10-phenanthroline) -  $Fe^{II}$  (ferroin) and  $CN^-$ . The extinction of the extract is measured at 597  $m\mu$  vs.  $CHCl_3$  as the reference soln. A standard deviation of  $\pm 1.15\%$  (ten results) is quoted for samples containing 4 p.p.m. of  $CN^-$ . The effects of pH, buffer composition, temperature, reaction time and reagent concn. have been examined. Of possible interfering ions, only the following seriously affect recovery of  $CN^-$ — $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$  ( $>2$  p.p.m.),  $IO_4^-$  and  $S^{2-}$ . The reaction can be applied qualitatively. An identification limit of 2  $\mu$ g of  $CN^-$  and a concn. limit of 1 in  $1.5 \times 10^6$  is claimed, in the absence of interfering ions.

F. L. SELFE

**92. Effect of zinc on the determination of cyanide with phenolphthalein.** W. H. Fischer (Gen. Engng Lab., G.E. Co., Schenectady, N.Y., U.S.A.). *Science*, 1958, **128**, 86-87.—The method depending upon oxidation of phenolphthalein to phenolphthalein in the presence of a trace of cupric salt and cyanide is subject to interference by Zn. Addition of increasing amounts of Zn produces an increase in absorption to a flat max. followed by a rapid fall to zero, the amount of Zn required for decolorisation being independent of the cyanide present. It is suggested that correction is possible by standardising the cyanide in the presence of the approx. amount of Zn present in the test soln.

H. F. W. KIRKPATRICK

**93. Rapid photometric titration of fluorosilicate in a chromium plating bath.** Soichiro Musha and Toshimasa Higashino (Fac. of Engng, Univ. of Osaka Prefecture, Sakai). *Japan Analyst*, 1958, **7** (3), 156-162.—The titration of  $SiF_6^{2-}$  (2 to 12 g per litre) with  $Th(NO_3)_4$  was studied, with the use of Fe salicylate (5 mM) as indicator. At pH 2.8, the extinction of Fe salicylate reaches a max. at the end-point and remains constant on further addition of  $Th^{4+}$ . To maintain the  $SiO_2$  and  $ThF_4$  in a colloidal condition, a surfactant is added. No interference results from  $Cr^{3+}$  ( $<10$  g per litre),  $Fe$  ( $<10$  g) or  $Cr_2O_7^{2-}$ . The error is  $<2\%$  and the time taken for an estimation is  $\approx 20$  min. **Procedure**—Filter the sample (10 ml), adjust the pH to 3.0 with NaOH and dilute to 100 ml. To a 10-ml aliquot add chloroacetic acid (1.5 M, adjusted to pH 2.8 with NaOH) (5 ml), Fe salicylate soln. (2 ml) (or, in the presence of Fe, 1.2 ml of 0.03 M Na salicylate) and the surfactant (e.g., 2% polyoxyethylene sorbitan laurate, 2 ml). Titrate the product with 0.25 M  $Th(NO_3)_4$ . In the presence of a large amount of Fe, the extinction of Fe salicylate is decreased with 0.1 M EDTA.

K. SAITO

**94. Determination of germanium by the heteropoly blue method.** E. R. Shaw and J. F. Corwin (Dept. of Chem., Antioch Coll., Yellow Springs, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1314-1316.—

**Procedure**—Neutralise the sample soln. and transfer an aliquot to a 100-ml flask containing 4 N  $H_2SO_4$  (2 ml) and wash down the sides with water to make 36 ml. Add 5% ammonium molybdate soln. (8 ml) and mix. In  $1.0 \pm 0.2$  min. add rapidly 50 ml of ferrous ammonium sulphate reductant (prep. described), dilute to the mark and mix. After 20 to 30 min. measure the extinction at 825  $m\mu$ . Provided that the concn. of  $GeO_2$  in the final soln. is between 0.1 and 0.3 mg per 100 ml, results are satisfactory. The effect of other variables on colour development is discussed.

F. L. SELFE

**95. Spectrophotometric studies on organometallic complexes used in analytical chemistry. III. Spectrophotometric determination of germanium with quercetinsulphonic acid.** Takuji Kanno (Res. Inst. for Dressing and Metallurgy, Tohoku Univ., Nagamachi, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (3), 306-310.—Quercetinsulphonic acid (3:5:7:3':4'-pentahydroxyflavone-6'-sulphonic acid) (I) (sol. in water) forms a sol. complex with Ge in a molar ratio of 1 to 3, both in acid and neutral soln., the max. absorption being at 400 and 450  $m\mu$ , respectively. The working curve is linear for  $<1$   $\mu$ g of Ge per ml at pH 5.6 to 6.2 (phosphate buffer). Hydrochloric acid distillate containing Ge is neutralised with aq.  $NH_3$  soln., mixed with buffer and aq. I soln. to make the concn. of I  $\approx 4 \times 10^{-4}$  M. The extinction is measured at 400  $m\mu$  against a reference soln. containing the same amount of I and  $NH_4Cl$ .

**IV. Reaction between germanium and flavonoid compounds.** Takuji Kanno. *Ibid.*, 1958, **79** (3), 310-314.—The reaction between germanium and flavonoid compounds was spectrophotometrically examined at various pH values to find the functional group for Ge. In a strong acid soln., those compounds having a hydroxyl group in the 3-position (e.g., quercetin, morin, 3-hydroxyflavone and 3-hydroxy-4'-methoxyflavone) are active. The max. absorption of the complex appears at 424 to 470  $m\mu$ . On the other hand, those compounds having a hydroxyl group in the 4'-position (e.g., hesperidin and luteolin) fail to give a complex. In neutral soln., those compounds having hydroxyl groups in both the 3'- and 4'-positions (e.g., quercetin and luteolin) are active, and the max. absorption appears at 396 to 408  $m\mu$ . The germanium complexes formed in acid and neutral soln. appear to have different characteristics.

K. SAITO

**96. Determination of small amounts of germanium in ores and minerals.** S. A. Dekhtrikyan. *Izv. Akad. Nauk ArmSSR, Ser. Geol. i Geogr. Nauk*, 1957, **10** (4), 121-128; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,034.—The earlier described method for the determination of Ge as molybdo-germanic heteropoly acid (Alimarin and Ivanov-Emin, *Zhur. Prikl. Khim.*, 1936, **9**, 1334) together with the separation of Ge by extraction of  $GeCl_4$  with  $CCl_4$  is used in the analysis of certain ores. **Procedure**—After decomposition of the ore by fusion, co-precipitate Ge with  $Fe(OH)_3$ . Filter off the ppt., wash it 4 or 5 times with water, dissolve it in  $HCl$  (4:1), and extract the  $GeCl_4$  with one 20-ml portion of  $CCl_4$  and two 15-ml portions for 2 to 5 min. Wash the  $CCl_4$  layer with two 10-ml portions of  $HCl$  (4:1) and extract the Ge with two 5-ml portions of water. To the resulting soln. add 2 to 4 ml of a 5% soln. of  $(NH_4)_2MoO_4$  and 2 ml of 2 N  $H_2SO_4$ , make up to 25 ml and measure the extinction. From 0.001 to 0.0003% of Ge may be determined.

C. D. KOPKIN

97. **New rapid gravimetric method for the macro-, semi-micro- and micro-determination of lead with organic reagents.** E. Popper, L. Popa, V. Junie and L. Roman (Fac. of Pharmacy, Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1957, **8** (3-4), 269-279.—In a soln. containing 0.05 to 0.2 g of  $Pb^{2+}$ , the macro-method with 1-phenylthiocarbamoyl-2-thiocarbamoylhydrazine or the monoallyl compound is recommended. For more dil. soln., the mononaphthyl derivative is recommended. *Procedure*—To a neutral or weakly acid (acetic) soln. of Pb diluted with ethanol (96%), warmed on a water bath, a warmed alcoholic soln. of the reagent is added gradually, with continuous stirring. The yellow crystalline ppt. settles in 5 min., is filtered off immediately, washed with warm ethanol (50%) and then with 3 to 5 ml of ethanol (96%) and 3 ml of ether, and dried *in vacuo*. The sensitivity of the method is 5  $\mu$ g per ml. Alkali metals and alkaline-earth metals do not interfere. H. SHER

98. **Separation of small amounts of lead by reductive ignition in a vacuum.** Z. A. Baskova and G. I. Novikov. *Geokhimiya*, 1957, (7), 580-583; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,361.—The possibility is established of separating small amounts of Pb from natural products by reductive ignition *in vacuo* at 1050° to 1100° in the presence of carbon as reducing agent. Carefully grind 3 to 5 g of sample with 3 to 4 g of carbon (spectrally pure carbon is first ignited at 1000° to 1100° in a stream of hydrogen or  $CCl_4$  to remove possible traces of Pb) and place in a quartz dish. Place the dish in a quartz tube sealed at one end, and connected to a vacuum pump ( $10^{-1}$  to  $10^{-4}$  mm Hg). On heating, the appearance of a grey deposit of sublimed metal commences between  $\approx 700^\circ$  and  $800^\circ$ , and heating the sample at 1050° to 1100° is accompanied by the formation of a copious deposit during 20 to 30 min. Keep the sample at the indicated temperature for 1.5 to 2.5 hr., then cool the tube and extract the Pb by leaching with a small amount of  $HNO_3$  (1:1), and determine Pb in the resulting soln. polarographically or photometrically. The results of the determination of Pb in various granitoids show that the method gives a separation of >90% of the Pb from rocks containing  $\approx 10^{-3}$  % of Pb. C. D. KOPKIN

99. **Quantitative determination of lead, iron and aluminium by drop-time potentiometry.** A. K. Kal'e and I. E. Ioshpa. *Trudy Gor'kovsk. Politekh. Inst.*, 1957, **13** (5), 50-55; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,403.—The possibility is established of using the earlier described (Kal'e, *Zavod. Lab.*, 1946, **12**, 773; 1947, **13**, 413) method of drop-time potentiometry for the determination of  $Pb^{2+}$  (titration with  $K_2CrO_4$  soln.),  $Fe^{3+}$  and  $Al^{3+}$  (titration with NaOH soln.). Slight changes which have been made in the apparatus to improve the contact between the cadmium electrode and the galvanometer terminal are described. It is established that the titration of  $Pb^{2+}$  can be carried out in weakly acid aq. medium: dilute 0.1 N Pb acetate, containing 15 ml of glacial acetic acid per litre, ten times, make up an aliquot of the resulting soln. to 55-1 ml and titrate with  $K_2CrO_4$  soln. till a distinct inflection is obtained on the time vs. concn. of  $Pb^{2+}$  curve. The error in determining  $Pb^{2+}$  is  $\pm 0.78$  to 0.95 mg. In titrating  $Fe(NO_3)_3$  or  $Al(NO_3)_3$  with 0.1 N NaOH the error is  $\pm 0.14$  mg. In all the described cases there is no direct proportionality between the amount of ion being titrated and the titration time up to the inflection point, which is

explained by the authors as being due to the disproportionately large decrease in the ionic strength of the soln. on pptn. of  $Fe^{3+}$ ,  $Pb^{2+}$  and  $Al^{3+}$ .

C. D. KOPKIN

100. **Polarographic determination of lead in tin-base alloys.** M. Ariel and P. Enoch (Dept. of Chem., Inst. of Technol., Haifa, Israel). *Anal. Chim. Acta*, 1958, **18** (4), 339-344.—If M NaOH is used as supporting electrolyte, Sn and Sb are not reduced at the dropping-mercury electrode, and most of the Cu is pptd., the remainder being reduced at  $-0.35$  V before the plumbite ion. Except, therefore, when the residual Cu exceeds the Pb, no separations are required. *Procedure* for 2 to 20% of Pb—The sample (100 mg) is dissolved in conc. HCl (2 ml) with dropwise addition of 30%  $H_2O_2$  (2 ml). After boiling the soln. to oxidise Sn and destroy excess of  $H_2O_2$ , 20 ml of 2 M NaOH and 0.2 ml of 0.5% gelatin soln. are added, the soln. is made up to 50 ml and polarographed between  $-0.6$  and  $-1.0$  V vs. the S.C.E. The sensitivity of the recorder is adjusted according to the amount of Pb present, and residual current compensated as far as possible. The diffusion current is measured at  $-0.9$  V by taking the peaks of the wave due to Pb and the extrapolated plateau due to Cu, and Pb is obtained by reference to a calibration curve prepared from soln. containing Pb and Cu. A determination occupies 30 min. *Procedure* for 0.4 to 2.0% of Pb—The sample (500 mg) is dissolved as before and, after destruction of  $H_2O_2$ , 20 ml of 4 M NaOH is added and water to 50 ml. The mixture is boiled, a few drops of 0.1 M  $Cu(NO_3)_2$  are added, and boiling is continued till the vol. is reduced to 20 ml. The  $CuO$  is filtered off on sintered glass or asbestos, the filtrate and washings are made up to 50 ml after addition of gelatin soln., and Pb is determined as before. A determination takes 1 hr. Results are good, the error not exceeding  $\pm 4\%$  of the Pb. R. E. ESSERY

101. **Determination of lead in molybdenum concentrates and industrial products.** Yu. K. Kedrova. *Sb. Nauch. Trud., Gos. Nauch. Inst. Tsvet. Met.*, 1958, (14), 21-28; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,391.—The following methods may be used for determining Pb in products containing considerable amounts of molybdenum sulphide in the absence of Ba—at concn. of 0.01 to 5% of Pb, the polarographic method without preliminary separation of Pb; with a content of Pb of  $<0.01\%$ , the chromate method of pptn. of Pb in dilute  $HNO_3$  and pptn. in an acetate buffer soln. (after separation of Pb as  $PbSO_4$ ); and with  $<0.5\%$  of Pb, the molybdate method. For products containing Ba, only the chromate method of pptn. in dilute  $HNO_3$  is recommended. If oxidised forms of Mo are present, use the polarographic method, with preliminary separation of Pb as  $PbSO_4$  or as the basic salt with  $Fe(OH)_3$ . In the analysis of samples containing up to 5% of Pb and in the absence of oxidised Mo, the polarographic method, after dissolution of the sample in HCl (2:1), is preferred as being the simplest and most rapid. C. D. KOPKIN

102. **Spectrographic analysis of lead pigments, lead oxides and metallic lead.** E. J. Dunn, jun., and J. P. Cestaro (National Lead Co., Brooklyn, New York). *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1958, **30**, 183-188.—An emission-spectrographic method for the analysis of 20 possible metallic contaminants in lead and its compounds has been developed. Lead oxide standards are used and the



procedure may be applied to metallic lead, PbO or lead pigments. The appearance or disappearance of impurities may thus be followed throughout the manufacture of a pigment. Particular features of the method are the establishment of complete burning, the use of weighed amounts of sample, dilution of the samples with an equal wt. of pure carbon dust, and the use of a hot-rod thin-walled carbon anode.

L. A. O'NEILL

**103. Micro-detection of titanium with  $\beta$ -diketone reagents.** Morizo Ishidate, Yasuhiro Yamane and Tazuko Tamano (Fac. of Pharm., Tokyo Univ., Hongo). *Japan Analyst*, 1958, **7** (3), 170-174.—Whereas  $Ti^{3+}$  in 0.2 to 4 N HCl give a green colour with  $\beta$ -diketones (but red with acetylacetone),  $Ti^{4+}$  give a yellow colour. For  $Ti^{3+}$ , acetylacetone is the most sensitive reagent (limit of detection, 1  $\mu$ g) and, for  $Ti^{4+}$ , *o*- and *m*-methoxydibenzoylmethane are most sensitive ( $\approx 0.25 \mu$ g). In 2 N HCl, interference of other ions is rarely observed;  $F^-$  should be masked with  $BeCl_2$  soln. (2.5%, 1 drop), and  $Fe^{3+}$  reduced to  $Fe^{2+}$  with zinc amalgam.

K. SAITO

**104. Polarographic determination of copper, cadmium, nickel, zinc, tin and antimony in metallic titanium.** T. V. Aref'eva and A. A. Pozdnyakova. *Sb. Nauch. Trud., Gos. Nauch. Inst. Tsvet. Met.*, 1958, (14), 67-73; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,429.—A new polarographic method is evolved for the determination of a series of impurities in metallic titanium, after their separation from the main mass of Ti by extraction, with ethyl acetate, as diethyldithiocarbamates. Polarograph Cu, Cd, Ni and Zn in a basal soln. of ammoniacal  $(NH_4)_2S$  at a concn. of  $<0.0005\%$  of each metal. Polarograph Sn and Sb in a basal soln. of 6 N HCl at a concn. of metal of  $<0.001\%$ . Concn. of 0.0001 to 0.01% of the indicated elements in a 1- to 2-g sample of metallic titanium can be determined, a semi-micro electrolyser with an external anode being used for the polarography. The reproducibility of the results is 25%.

C. D. KOPKIN

**105. A potential source of sampling error in the determination of nitrogen in titanium alloys.** J. D. Hobson and D. Swinburn (Hadfields Ltd., East Hecla Works, Sheffield, England). *Analyst*, 1958, **83**, 376-377.—Erratic results during experimental work on the segregation of nitrogen in large billets of titanium alloys suggested serious contamination with atmospheric nitrogen during preparation of samples by milling or drilling. The nitrogen content was determined of samples prepared by different methods, with variations in the kind of sampling tool, its speed and the cutting speed. Quoted results showed that it is essential to drill at low speeds with a relatively coarse feed and a freshly sharpened drill if contamination of the sample with nitrogen is to be avoided.

A. O. JONES

**106. Analysis for industry [separation and determination of thorium with organic acids. I, II].** W. I. Stephen. *Ind. Chem. Mfr*, 1958, **34**, 254-256; 393-395.—The merits of the various org. acids that have been advocated for use in the determination of Th are compared. (59 references.)

S.C.I. ABSTR.

**107. Determination of small amounts of thorium with quercetin.** I. P. Alimarin, A. P. Golovina and A. F. Kutelnikov. *Byull. Nauch.-Tekh. Inform.*

*Min. Geol. i Okhran' Nedr. SSSR*, 1957, [7(12)], 61-64; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,431.

—Quercetin (I) forms with  $Th^{4+}$  a yellow-green complex, the intensity of the colour being proportional to the concn. of Th. The colour of soln. of this complex is stable for 20 to 30 hr.; on long standing ( $>48$  hr.) a green-brown ppt. separates, which is soluble in ethanol and methanol. The coloured soln. of the complex may be stabilised by the addition of up to 40% of ethanol or a 1% soln. of gelatin. The complex formed by  $Th^{4+}$  with I is readily extracted with isoamyl alcohol (at pH  $\approx 6.5$  up to 97.7% of the Th is extracted), cyclohexanone (at pH  $\approx 7$ , 93.5% of the Th is extracted), *n*-butanol and amyl acetate. For the photometric determination of  $Th^{4+}$ , to the soln. containing 0.0025 to 0.225 mg of Th add 5 or 10 ml of acetate buffer soln. (pH  $\approx 4$ ), 10 ml of ethanol and 2 ml of a 0.1% ethanolic soln. of I, set aside for 20 min., make up to 25 ml and measure the extinction at 455  $m\mu$  against water as comparison soln. To determine 0.0001 to 0.001 mg of Th per ml, use 0.2 ml of the soln. of I. A method is described for the removal of Th from Ce, based on extraction of the complex of  $Th^{4+}$  with I by means of isoamyl alcohol.

C. D. KOPKIN

**108. Separation of thorium from rare earths.** T. Suryanarayana Murthy and D. V. N. Sarma (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1958, **161** (2), 114-115 (in English).—The procedure described is recommended for the determination of Th in a soln. of the nitrates derived from monazite. To 10 ml of soln. containing  $\approx 70$  mg of  $ThO_2$  add N EDTA (disodium salt) (20 ml), 5% 8-hydroxyquinoline (I) soln. in dil. acetic acid (12 ml) and 5% aq.  $NH_4NO_3$  soln. (5 ml) in that order. Dilute the soln. to 100 ml and heat to 90°. Make just alkaline with NaOH after heating for 15 min., cool, and filter. Wash the ppt. with I soln. and dissolve it in  $\approx 100$  ml of HCl (1:1). Add 5 ml of EDTA soln., heat the soln. to 90° and make just alkaline with NaOH. Wash the ppt. with I soln. followed by dil. aq.  $NH_3$ , dry, ignite, and weigh as  $ThO_2$ . The greatest error shown in 4 determinations is 0.2 mg.

G. BURGER

**109. Colorimetric determination of thorium in ores with compensation for complex formation.** A. F. Kutelnikov and G. A. Lanskoj. *Byull. Nauch.-Tekh. Inform. Min. Geol. i Okhran' Nedr. SSSR*, 1957, [4(9)], 76-78; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,432.—In the determination of Th with arsenazo (I) as reagent, the intensity of the colour of the complex of Th with I is weakened in the presence of accompanying complex-forming ions ( $IO_3^-$ ,  $C_2O_4^{2-}$ ,  $F^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ , etc.), which leads to an error of up to 20 or 30% in the determination of Th. To eliminate this error the use of two aliquots of the soln. for the determination of Th with I is recommended. Introduce equal quantities of the soln. into each of two identical volumetric flasks, and add to one of them a ml of a standard soln. of  $Th^{4+}$ , which corresponds, from a calibration curve, to an optical density  $D_0$ . Add to each flask an equal quantity of I, make up to the marks and measure the optical densities of the two soln.,  $D_1$  and  $D_2$ . Because of complex formation these values will be less than would be obtained from pure soln. of Th. The ratio  $(D_1 - D_2)/D_0$  indicates the quantity of  $Th^{4+}$  combined with I. If from the calibration curve the value  $D_1$  corresponds to  $x$  g of Th, then the actual content of Th, ( $y\%$ ), is found from the formula  $y = x \cdot D_0 \cdot P \cdot 100 / (D_1 - D_2) \cdot H$ .



where  $H$  is the wt. of sample in g, and  $P$  is the dilution factor. The procedure may be used for the photometric determination of Th in natural samples, with the natural ratio of Th to rare-earth elements, after pptn. of the oxalates of Th and the rare earths and their conversion into the nitrates. The results obtained agree well with the data obtained by the photometric back-titration with thoron.

C. D. KOPKIN

**110. The analysis of thorium-indium alloys.** G. W. C. Milner and J. W. Edwards (A.E.R.E., Harwell, England). A.E.R.E. Report C/R 2613, 1958, 6 pp.—The alloy is dissolved in  $\text{HNO}_3$  plus a small amount of sodium fluorosilicate, and after fuming the soln. to dryness with  $\text{HClO}_4$  the residue is dissolved in  $\text{H}_2\text{O}$  and the soln. made up to vol. Indium is quant. separated from an aliquot ( $\approx 100$  mg of Th or In) by extraction into isobutyl methyl ketone from a soln. containing 0.5 M NaI and  $\text{M HClO}_4$ . The Th in the aq. phase is determined by diluting the soln. to  $\approx 125$  ml, adding a small amount of ascorbic acid and slowly titrating the soln. (adjusted to pH 2.5 to 3) with 0.05 or 0.005 M EDTA (disodium salt) until the colour of the indicator (0.1% xylenol orange) changes to pure yellow. The In in the organic phase is determined by adding  $\approx 100$  ml of  $\text{H}_2\text{O}$ , 10% aq. ammonium acetate soln. (10 ml) and a small amount of sodium metabisulphite and stirring vigorously. The pH of the aq. layer is adjusted to pH 3 to 3.5 (dil.  $\text{HClO}_4$ ), and the back-extracted In is titrated slowly with EDTA and the same indicator. The accuracy is high for either element.

W. J. BAKER

**111. Separation of thorium and rare-earth elements in nitric acid media by anion exchange.** J. Danon (Escola Nac. de Quím., Avenida Pasteur 404, Rio de Janeiro, Brazil). *J. Inorg. Nuclear Chem.*, 1958, 5 (3), 237-239.—Praseodymium-143 was eluted from a column of Dowex 1, 8% DVB, 50 to 100 mesh ( $\text{NO}_3$  form), with 5 M  $\text{HNO}_3$ , then  $^{234}\text{Th}$  was eluted with 2.4 M HCl. Samarium (100  $\mu\text{g}$ ) was similarly separated from Th (40 mg) by using 7.3 M  $\text{HNO}_3$  and 2.4 M HCl.

G. J. HUNTER

**112. Determinations of thorium and uranium in sedimentary rocks by two independent methods.** J. A. S. Adams, J. E. Richardson and C. C. Templeton (Shell Development Co., Houston, Texas). *Geochim. et Cosmoch. Acta*, 1958, 13 (4), 270-279.—One method for the determination of down to 1 p.p.m. of Th or U in common rocks is based on total  $\alpha$ -activity measurements combined with fluorimetric determinations of U. The  $\alpha$ -activity is measured in a proportional counter, the powdered rock sample having a surface area of  $\approx 20$  sq. cm. From the ratio of the  $\alpha$ -activity to the concn. of U determined fluorimetrically, the Th to U ratio can be found. In an independent method for determining the Th to U ratio by  $\gamma$ -ray spectral analysis, large thallium-activated sodium iodide scintillation crystals are used, with heavy shielding, and spectral energies 1.76 MeV from  $^{214}\text{Bi}$  in the uranium series and 2.62 MeV from  $^{208}\text{Tl}$  in the thorium series. When secular radioactive equilibrium exists in well-homogenised samples, results of both methods agree to within the experimental errors.

R. A. HOWIE

**113. Determination of the nitrogen of ammonium salts by the formaldehyde method.** L. M. Kontorovich, I. G. Solov'eva and G. T. Levchenko. *Gos.*

*Nauch. i Proektn. Inst. Azotn. Prom.*, 1957, (8), 243-245; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,409.—It is established that the formaldehyde method of determining ammoniacal N, based on the titration of the free acid formed on treating the ammonium salt with formaldehyde soln. (40%) (I), gives low results (on the average low by 0.65%). This error is explained by the formation of Na formate on neutralising I with NaOH, which hydrolyses on subsequent dilution with the formation of free  $\text{NaOH}$ , which reduces the NaOH titre. The following method is proposed to remove this error. Dilute 10 or 15 ml of I to 100 ml, add 2 or 3 drops of phenolphthalein and neutralise with 0.5 N NaOH; dissolve the sample in the resulting neutral soln. and after 1 or 2 min. titrate with 0.5 N NaOH. The accuracy of the results obtained is confirmed by the analysis of chemically pure  $\text{NH}_4\text{NO}_3$ .

C. D. KOPKIN

**114. Volumetric determinations with bromate. II. Determination of hydrazine with potassium bromate solution.** L. Szekeres, E. Sugár and É. Pap (Landwirtschaftlichen Univ., Budapest). *Z. anal. Chem.*, 1958, 161 (1), 38-40.—Hydrazine can be titrated in N HCl soln. at room temp. with 0.1 N  $\text{KBrO}_3$  in the presence of 1 drop of 0.1 N KBr and 1 ml of starch soln. The blue colour is discharged at the end-point.

G. BURGER

**115. Inorganic nitrogen compounds. III. Paper-electrophoretic separation of inorganic nitrogen compounds.** J. Vepřek-Šiška, F. Smirnov, V. Pliška and F. Veselý (Inst. Inorg. Chem., High-School of Chem. Technol., Prague). *Chem. Listy*, 1958, 52 (3), 410-412.—Procedure—Place 1  $\mu\text{l}$  of the mixture containing  $\text{NH}_4\text{Cl}$ , hydroxylamine hydrochloride, hydrazine hydrochloride,  $\text{N}_2\text{O}_3^{2-}$ ,  $\text{N}_2\text{O}_4^{2-}$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  in 0.001 N NaOH on each of three strips of chromatographic Whatman paper No. 1 (56 cm  $\times$  8 cm) and separate the compounds by means of electrophoresis with a different electrolyte for each of the strips. For the separation of  $\text{NH}_4^+$ , hydroxylamine and hydrazine, 0.001 N  $\text{H}_2\text{SO}_4$  is used and the detection made with  $\text{K}_2\text{HgI}_4$  soln. (0.5% soln. in 2.5% NaOH soln.);  $\text{NH}_4^+$  yield a yellow or brown spot, and a grey or black spot of reduced Hg indicates the presence of hydroxylamine or hydrazine. For the separation of  $\text{N}_2\text{O}_3^{2-}$  from  $\text{N}_2\text{O}_4^{2-}$ , an alkaline soln. of  $\text{Na}_2\text{SO}_4$  (15 g of  $\text{Na}_2\text{SO}_4$  and 0.6 g of NaOH in 1 litre) is used as electrolyte, and 1  $\mu\text{l}$  of  $\text{FeCl}_3$  soln. (5%) and 1  $\mu\text{l}$  of aq.  $\text{NH}_3$  (10%) are placed at the origin on the paper strip. For the detection,  $\text{AgNO}_3$  soln. (1%) is used, and the paper is illuminated with u.v. light (5 min.) filtered with a UG 4 filter. With  $\text{N}_2\text{O}_3^{2-}$ , the black spot of reduced Ag appears immediately after the paper has been moistened with the reagent, that due to  $\text{N}_2\text{O}_4^{2-}$  appears after the illumination. The presence of  $\text{FeCl}_3$  enables  $\text{N}_2\text{O}_3^{2-}$  to be separated from  $\text{N}_2\text{O}_4^{2-}$  as a result of the formation of a complexing anion with  $\text{N}_2\text{O}_4^{2-}$ . Nitrates and nitrites are separated in  $\text{Na}_2\text{SO}_4$  soln. (15 g of  $\text{Na}_2\text{SO}_4$  in 1 litre) satd. with  $\text{Ag}_2\text{SO}_4$ , and detected with KI soln. (1%) containing 0.5% of starch; after a short exposure (5 to 30 sec.) to u.v. light, a violet spot due to  $\text{NO}_2^-$  appears; the appearance of a similar spot after moistening the paper with acetic acid soln. (5%) indicates the presence of  $\text{NO}_3^-$ .

J. ZÝKA

**116. New methods for the determination and detection of phosphorus on a micro-analytical scale.** F. Lucena-Conde and A. Martinez de Pancorbo

(Univ. of Salamanca, Spain). *Acta Salamanticensis, Serie de Ciencias*, 1958, **2** (3), 15 pp. (in English).—From 0.10 to 10  $\mu\text{g}$  of  $\text{PO}_4^{3-}$  in 10 ml of soln., e.g., of a biological sample, can be rapidly determined by adding 1 ml of the Lucena - Prat reagent (cf. *Anal. Abstr.*, 1957, **4**, 3911) followed by 5 ml of  $\text{H}_2\text{O}$  and heating the mixture for 15 min. at 100° (steam bath) to develop the blue colour. The extinction of 1 ml of the rapidly cooled soln. is then measured spectrophotometrically at 830  $\text{m}\mu$  against  $\text{H}_2\text{O}$  as reference. Beer's law is valid. Provided that  $\text{AsO}_4^{3-}$ ,  $\text{GeO}_4^{3-}$  and  $\text{SiO}_4^{2-}$  are absent, the reagent (an acid mixture of ammonium molybdate and  $\text{MoCl}_5$ , preferably having the ratio of  $\text{Mo}^{6+}$  to  $\text{Mo}^{5+}$  of 3:2) can also be used for the detection of microgram amounts of  $\text{PO}_4^{3-}$  in soln. at pH 5.3. The following anions interfere— $\text{IO}_3^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{F}^-$  and  $\text{SO}_3^{2-}$ , and  $\text{SCN}^-$  (>100  $\mu\text{g}$ ). If the concn. of  $\text{PO}_4^{3-}$  is between 5 and 0.5  $\mu\text{g}$  per ml, the blue colour is best revealed by extraction of the soln. with *n*-butanol at pH 6.3. (Cf. Prat Perez, *Anal. Abstr.*, 1957, **4**, 2163.) W. J. BAKER

**117. Colorimetric determination of phosphorus.** D. N. Fogg and N. T. Wilkinson (I.C.I. Ltd., Res. Dept., Alkali Div., Winnington, Northwich, Ches., England). *Analyst*, 1958, **83**, 406-414.—The method described is based on that of Denigès (*Compt. Rend.*, 1920, **171**, 802), but the molybdophosphate is reduced with ascorbic acid instead of with  $\text{SnCl}_2$ . Stated amounts of Fe, Cl $^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  and sol.  $\text{SiO}_2$  can be tolerated. Arsenate interferes by yielding the same colour, but when reduced to arsenite 0.01 g of As has no effect. Organic matter can be removed by wet oxidation, and interfering amounts of Cl $^-$  and  $\text{NO}_3^-$  may be removed by evaporation with  $\text{H}_2\text{SO}_4$  and subsequent neutralisation of the soln. Applications of the method to the determination of  $\text{P}_2\text{O}_5$  in boiler water, effluents and salt deposits are described. A. O. JONES

**118. Amperometric determination of phosphorus in metallurgical materials.** T. Chlebovský (Hutn. Fak., Vysoká Škola Báňská, Ostrava, Czechoslovakia). *Hutn. Listy*, 1958, **13** (3), 252-253.—The polarographic behaviour of  $\text{Mo}^{\text{V}}$  and  $\text{Mo}^{\text{III}}$  was studied and conditions for the amperometric titration of  $\text{Mo}^{\text{III}}$  with  $\text{FeCl}_3$  soln. have been found. An indirect determination of P has been developed. *Procedure for phosphorus in minerals, iron and steel*—Dissolve the sample (0.25 to 5 g) ( $\approx 0.1$  to >1% of P) in  $\text{HNO}_3$  (1:1) (20 to 100 ml) by heating. Evaporate, and dry the residue at 130° (0.5 to 1 hr.), then moisten it with conc. HCl (10 to 20 ml), add hot water (50 ml), and filter off and wash the  $\text{SiO}_2$ . Evaporate the filtrate to 20 or 50 ml, add 10  $\text{N}$   $\text{H}_2\text{SO}_4$  (2 ml), warm slightly, then cool. Transfer to a separating funnel, add ammonium molybdate soln. (10% in  $\text{N}$   $\text{H}_2\text{SO}_4$ ) (2 to 5 ml) and isobutyl alcohol (10 ml). Shake for 1 to 2 min., separate the alcoholic phase and repeat the shaking twice with 5 ml of isobutyl alcohol. Combine the alcoholic phases, wash with  $\text{N}$   $\text{H}_2\text{SO}_4$ , add NaOH (2 g) and a few ml of  $\text{H}_2\text{O}$ . Separate the aq. phase, neutralise with HCl, place in the separating funnel, and add zinc amalgam and HCl to a concn. of 15 or 20%. Reduce to red  $\text{Mo}^{5+}$  by shaking, separate the amalgam, transfer the soln. containing the  $\text{Mo}^{5+}$  into a titration vessel containing 30 ml of oxygen-free water and titrate with 0.1  $\text{N}$   $\text{FeCl}_3$  with the use of amperometric control ( $E = -0.25$  V, dropping-mercury electrode). The interference of arsenates can be avoided by heating with HCl and

Br; vanadates must be reduced to  $\text{V}^{\text{IV}}$  with  $\text{FeSO}_4$  or  $\text{NaHSO}_4$  before the titration. J. ŽYKA

**119. A rapid colorimetric molybdenum blue method for phosphoric acid determination.** P. Kajanne (Lohja Kotka Oy, Lohja, Finland). *Suomen Kem. B.*, 1957, **30** (5-6), 101-108.—Ferrous ammonium sulphate (I) was found to be very satisfactory for reducing the complex molybdophosphoric acid to molybdenum blue when EDTA was used to complex the  $\text{Fe}^{2+}$  formed during the reduction. *Procedure*—Add to the sample (100 ml containing  $\approx 0.1$  mg of  $\text{P}_2\text{O}_5$ ) a soln. of ammonium molybdate (2% in 28%  $\text{H}_2\text{SO}_4$ ) (5 ml) and a soln. of I (8% in 0.2%  $\text{H}_2\text{SO}_4$ ) (2 ml). Set aside for 5 to 15 min., add an aq. soln. of 1.2% EDTA (disodium salt) (5 ml) and measure the absorbance after 1 to 2 min. against a test soln. containing all the reagents except ammonium molybdate (Evans colorimeter, red filter No. 609, 10-cm cell). There is no interference from  $\text{SiO}_2$  in concn. up to 100 times that of the  $\text{P}_2\text{O}_5$ . The method is recommended for the routine determinations of  $\text{H}_3\text{PO}_4$  in, for example, boiler-house waters. E. SJÖSTRÖM

**120. Photometric determination of phosphoric acid and silicic acid in a single solution.** II. E. Ruf (T. Goldschmidt A.-G., Essen). *Z. anal. Chem.*, 1958, **161** (1), 1-16.—After boiling the sample soln. with NaOH to depolymerise the silicic acid, sodium molybdate and 6  $\text{N}$  HCl (10 ml) are added and the soln. is made up to 50 ml. The molybdophosphoric acid is extracted with isobutyl alcohol and the extract is shaken with  $\text{SnCl}_4$  and  $\text{CHCl}_3$ . Molybdophosphorus blue forms and collects in the aq. layer. The extinction is measured at 700  $\text{m}\mu$ . The original aq. layer is neutralised with aq.  $\text{NH}_3$ , made just acid with HCl and a further 5 ml of 6  $\text{N}$  HCl is added. This soln. is shaken with  $\text{CHCl}_3$  and  $\text{SnCl}_4$  and the extinction of the molybdosilicic blue in the aq. layer is measured at 700  $\text{m}\mu$ . If ammonium molybdate is used in place of sodium molybdate, the soln. must be less acid and the pH ranges are more restricted. The procedure can be modified to enable  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  to be used instead of HCl. With appropriate pre-treatments, this method is applicable to such materials as misch metal, ferromanganese and fluorspar. No interference is caused by 1 g of Al, rare earths,  $\text{Cr}^{\text{III}}$ , Ni, Mg, Ca, Sr, Ba, Li, Na or K. Interference by Zr, Ti and  $\text{Cr}^{\text{VI}}$  can be avoided; As interferes with the determination of P, and Fe with the Si. The permissible amounts of F (50 mg for P and 20 mg for Si) can be increased in the presence of Al. These amounts are based on 100  $\mu\text{g}$  of Si or P. G. BURGER

**121. Polarographic determination of arsenic in lead.** Hidehiro Gotō and Shigeru Ikeda (Tohoku Univ., Sendai, Japan). *Sci. Rep. Res. Inst., Tohoku Univ.*, A, 1957, **9**, 91-96.—*Procedure*—Dissolve 10 g of lead metal in 50 ml of  $\text{HNO}_3$  (1:4), cool, and precipitate the Pb as sulphate with 20 ml of  $\text{H}_2\text{SO}_4$  (1:3). Filter off and wash the ppt. Evaporate the filtrate to fumes of  $\text{H}_2\text{SO}_4$  and, after residual  $\text{HNO}_3$  is liberated, add 0.5 g of hydrazine sulphate. Cool the soln. and transfer to a 100-ml flask. Two polarographic methods are available for measurement. (i) Dilute 50 ml of ethanol, 10 ml of 5  $\text{N}$  acetic acid, and 0.1% gelatin to 100 ml with water. Transfer 5 ml to a cell and pass H through for 20 min. Arsenic is determined by measuring the wave height at the potential from -0.6 to 0.8 V. There is no interference from <1 mg per 100 ml of Fe, Bi, Sb, Sn, Cu, Pb or Zn.

(ii) Make the soln. (100 ml) *M* with  $\text{MnSO}_4$  and *N* with  $\text{H}_2\text{SO}_4$ . Pass *H* through the soln. as described above and determine *As* by measuring the wave height at the potential from  $-0.9$  to  $-1.2$  V. There is no interference from  $<5$  mg per 100 ml of Fe, Sb, Bi, Sn, Cu or Zn. The determination of 0.003 to 0.1% of *As* in lead metal is possible by either method.

CHEM. ABSTR.

**122. Comparative evaluation of colorimetric methods for the determination of bismuth.** E. P. Ozhigov, A. N. Dorokhina and I. I. Mirkina. *Soobshch. o Nauch.-Issled. Rabot. Chlenov Primorsk. Old. Vses. Khim. Obsch. im. D. I. Mendeleev*, 1957, (3), 79-87; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,444.—A comparison is made of two colorimetric methods (the iodide and the thiourea methods) for the determination of Bi as applied to ores and lead concentrates. Determine Bi in polymetallic ores and lead concentrates containing 0.005 to 0.7% of Bi and 3.97 to 5.16% of Fe (in an ore) or 1.47 to 2.40% of Fe (in a lead concentrate) by the colorimetric iodide method after pptn. of  $\text{PbSO}_4$  or, preferably, by the thiourea method without preliminary removal of Pb. In the latter case no interference is caused by the presence, in 100 ml of soln., of 30 mg of Cu, 20 mg of Pb and Zn, and small quantities of Ag, Hg, Cd and Sn; Sb may be complexed with tartaric acid. The ratio of Fe to Bi should be  $<100$  to 1. The thiourea method is more economical, more rapid and gives satisfactory reliable results.

C. D. KOPKIN

**123. Gravimetric determination of bismuth using hypophosphorous acid.** D. R. Bomberger (Univ. of Calif. Radiation Lab., Livermore, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1321-1322.—Prepare sample soln. containing 1 to 2 mg of Bi per ml in  $\text{N HClO}_4$  free from Cl $^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Add 1 ml of hypophosphorous acid (30% soln.) for each 20 ml of sample soln. Digest, just below boiling-point, for 1 to 2 hr., then pour the hot supernatant liquid through a fine sintered-glass filter-crucible. Wash the ppt. twice by decantation with water, transfer it to the crucible, wash with 95% ethanol and ether and dry at  $110^\circ$  for 0.5 to 1 hr. Cool and weigh the metallic bismuth. Interference is caused by those elements that are pptd. as salts of hypophosphorous acid, namely  $\text{Sc}^{III}$ ,  $\text{Zr}^{IV}$ ,  $\text{Hf}^{IV}$ ,  $\text{Th}^{IV}$  and Ta $^{IV}$ , and by Cu, Ag, Au, Hg, Sb, As, Se, Te and Pd, which are reduced to an insol. form, usually the element. There is no interference from Li $^+$ , Na $^+$ , K $^+$ , Mg $^{2+}$ , Ca $^{2+}$ , Zn $^{2+}$ , Ba $^{2+}$ , Al $^{3+}$ , Pb $^{2+}$ , Cr $^{3+}$ , Mn $^{2+}$ , Fe $^{3+}$ , Co $^{2+}$  or Ni $^{2+}$ . A  $\text{HClO}_4$  concn. of 0.1 *N* is used when K is present to prevent pptn. of  $\text{KClO}_4$ .

F. L. SELFE

**124. Amperometric titration of bismuth with potassium ferricyanide.** V. M. Babenyshev, A. Ya. Shchelkanovtseva and O. M. Kuznetsova. *Sb. Nauch. Trud. Kuibyshevsk. Ind. Inst.*, 1957, (7), 37-43; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,383.—The pptn. of Bi with  $\text{K}_3\text{Fe}(\text{CN})_6$  is studied amperometrically. It is established that the ppt. formed in the titration has the composition  $\text{BiFe}(\text{CN})_6$ , and is somewhat soluble close to the equivalence point. The amperometric determination of Bi with  $\text{K}_3\text{Fe}(\text{CN})_6$  is possible in dilute  $\text{HNO}_3$  soln. at concn. of Bi of 0.01 to 0.003 *M* with an accuracy up to  $\pm 1\%$ . Metals that form ppt. with  $\text{K}_3\text{Fe}(\text{CN})_6$  interfere. The presence of up to 5% of  $\text{Al}(\text{NO}_3)_3$  is allowable; other anions interfere if they cause hydrolysis of the  $\text{Bi}(\text{NO}_3)_3$ .

C. D. KOPKIN

**125. Volumetric determination of bismuth. II. Titration of the trithiosulphate complex with standard alkali.** Yung-Chao Chen. *Acta Chim. Sinica*, 1957, **23** (5), 340-345 (from English summary).—Bismuth hydroxide can be converted into a trithiosulphatobismuth complex by adding a large excess of  $\text{Na}_2\text{S}_2\text{O}_3$  (I), followed by dilute  $\text{HNO}_3$  to dissolve the hydroxide. The complex can be titrated with NaOH soln.; the error is  $\pm 0.5\%$ . In the determination of 0.1 g of Bi the following ions do not interfere in the concn. shown; when an excess of I is necessary, this is indicated—Pb $^{2+}$  80 mg; Cr $^{3+}$  25 mg (15 g of I); Cu $^{2+}$  and Co $^{2+}$  100 mg; Fe $^{3+}$  80 mg; Zn $^{2+}$  40 mg; Ca $^{2+}$  200 mg; Ag $^+$  30 mg; Mo $^{6+}$  30 mg (10 g of I); Ni $^{2+}$  40 mg (10 g of I) or 40 to 60 mg (15 g of I), Cd and Mn. Arsenic (ter- and quinque-valent), Cl $^-$  and  $\text{SO}_4^{2-}$  interfere. These two anions form insoluble oxy-salts in dil.  $\text{HNO}_3$  and As must be removed at the outset; Sn, Sb and W should also be removed by treatment with conc.  $\text{HNO}_3$ . The complete titration takes 0.5 hr. and is suitable for the determination of Bi in ores.

S.C.I. ABSTR.

**126. Separation of vanadium from phosphorus on cation-exchange resins.** L. A. Kadushkina and E. A. Trukhina. *Trudy Inst. Khim. Nauk, Akad. Nauk KazSSR*, 1957, **1**, 86-94; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,401.—In a soln. containing salts of VV and phosphates, first reduce VV to VO $^{2+}$  by passing a stream of  $\text{SO}_2$  and pass the soln. through a column of cationite (SDV-3, SBS-R or KU-2); the VO $^{2+}$  are adsorbed, the phosphates passing through without loss. The dynamic and complete exchange capacity has been determined for KU-2 both for pure soln. of the components and for mixtures containing Na $^+$ , VO $^{2+}$  and phosphates. It is established that the described method completely removes phosphates from V. The presence of Na $^+$  and citric, tartaric and oxalic acids, and high acidity of the soln., causes considerable reduction in the adsorption of V.

C. D. KOPKIN

**127. Colorimetric determination of vanadium in bauxite and "red mud."** S. V. Zaleskaya. *Trudy Gor'kovsk. Politekh. Inst.*, 1957, **13** (5), 90-93; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,392.—In the determination of V in bauxite and red mud, use is made of Vinogradov's method (*Dokl. Akad. Nauk SSSR*, Ser. A, 1931, 10), based on the formation of yellow tungstovanadophosphate. It is established that NaOH is the best flux for getting the sample into solution; removal of  $\text{SiO}_2$  is not necessary. To determine V, fuse 1 g of sample with 5 g of NaOH, extract with water (50 ml), filter, wash the residue with 0.5%  $\text{Na}_2\text{CO}_3$  soln. and make the filtrate up to 100 ml. Neutralise 25 ml of this soln. with 6 *N*  $\text{H}_2\text{SO}_4$  to methyl orange, add 3 ml of the acid in excess and, while stirring, 0.5 ml of 1%  $\text{H}_2\text{O}_2$  and 4%  $\text{KMnO}_4$  soln. dropwise to a purple colour. Allow to stand for 25 min., add 1%  $\text{NaNO}_2$  soln. dropwise to decolorise the soln. and 1 drop in excess, followed by 2 ml of  $\text{H}_3\text{PO}_4$  (1:2) and 1 ml of a 15% soln. of  $\text{Na}_2\text{WO}_4$ . Make up to 50 ml and compare the colour of the soln. with that of a standard  $\text{NH}_4\text{VO}_3$  soln. containing 0.01 mg of V per ml. Satisfactory results are obtained.

C. D. KOPKIN

**128. Trihydroxyaurine as analytical reagent for metavanadate.** K'uei Wang. *Acta Chim. Sinica*, 1957, **23** (5), 346-350 (from English summary).—3:3':3"-Trihydroxyaurine gives a blue-black ppt. or blue colour with metavanadate. In a spot test, the identification limit is 0.007  $\mu\text{g}$ . Among the

cations and anions tested, Ag, Cu<sup>2+</sup>, Pb, Bi, Sn<sup>2+</sup>, Sn<sup>4+</sup>, Sb<sup>3+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> interfere. At pH < 5 the colour fades; at pH 7 to 9 the colour intensity attains a max., and at pH > 10 the colour fades owing to formation of V<sub>2</sub>O<sub>5</sub><sup>4-</sup>. After mixing the test soln. with the reagent, the max. colour intensity is attained in 25 min. Beer's law is obeyed for concn. of metavanadate < 1 µg per ml.

S.C.I. ABSTR.

129. Separation of niobium from zirconium by a cation exchanger. H. Sano and R. Shiomi (Dept. of Chem., Fac. of Sci., Univ. of Tokyo, Japan). *J. Inorg. Nuclear Chem.*, 1958, 5 (3), 251-252.—Carrier-free <sup>93</sup>Nb and <sup>90</sup>Zr were adsorbed from 0.1 N HCl on to a column of Dowex 50W-X8, 200 to 400 mesh (H form). The Nb was eluted with either 0.1 N or N HCl containing 0.3 or 3% H<sub>2</sub>O<sub>2</sub>, respectively, and the Zr was then eluted with 0.5% oxalic acid. G. J. HUNTER

130. Quantitative spectroscopic determination of niobium in titanium and zirconium minerals. L. S. Borodin. *Trudy Inst. Mineral., Geokhim. i Kristallokhim. Redk. Element., Akad. Nauk SSSR*, 1957, (1), 182-187; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,038.—A method is described for the determination of relatively large amounts (0.1 to 5%) of Nb in minerals, by excitation of the spectra in a d.c. arc discharge at 10 amp. with complete evaporation of 10 or 15 mg of sample in 4 or 5 min. Several types of standards on different bases are prepared by mixing Nb<sub>2</sub>O<sub>5</sub> with the minerals. The analysis is carried out with the lines 2671.9 and 2716.6 Å; the background serves as comparison element for the spectra which are photographed on a medium spectrograph. The calibration curves, constructed within the limits 0.2 to 0.6% of Nb, are displaced relative to one another depending on the nature of the base material taken for the preparation of the standards. The error of the analysis in the majority of cases is  $\pm 10\%$ . C. D. KOPKIN

131. Determination of niobium and tantalum in ores. I. I. Nazarenko. *Trudy Inst. Mineral., Geokhim. i Kristallokhim. Redk. Element., Akad. Nauk SSSR*, 1957, (1), 188-194; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,395.—It is established that, for the quant. separation of Nb with tannin before its photometric determination in ores by the thiocyanate method, it is expedient to use co-pptn. with gelatin (treat the sample, after decomposition with a mixture of HF and H<sub>2</sub>SO<sub>4</sub>, with a 1% soln. of tannin in 5% HCl with the addition of 1 ml of a 1% soln. of gelatin). In the analysis of ores containing 0.001 to 0.1% of Nb, a single tannin treatment is sufficient; in the determination of Ta (0.001 to 0.02%) with pyrogallol, a double tannin treatment is necessary, since in this case the presence of Ti causes interference in the determination of Ta. Results are given of the analysis of a large number of samples of minerals, ores and artificial mixtures.

C. D. KOPKIN

132. Spectrophotometric determination of a micro amount of sulphur by methylene blue-nitrobenzene extraction method. Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst.*, 1958, 7 (3), 181-184.—Methylene blue (I) is extracted from 0.1 to 0.5 N HCl soln. into nitrobenzene (II) or alcohols immiscible with water. In II, I gives a max. absorption at 668 mµ, which remains unchanged for 4 days; Beer's law is obeyed for < 25 µg of S per 25 ml.

Sulphate S is converted into H<sub>2</sub>S with SnCl<sub>2</sub> in conc. H<sub>3</sub>PO<sub>4</sub> (Kiba *et al.*, *Anal. Abstr.*, 1956, 3, 2708). The H<sub>2</sub>S is absorbed in CdSO<sub>4</sub> (0.1 M, 30 ml) and treated with *p*-aminodimethylaniline soln. (0.1%, 15 ml), FeCl<sub>3</sub> (0.02 M, 3 ml) and HCl (1.9 N, 12 ml). After 30 min., the product is mixed with NaOH (2.27 N, 14 ml), diluted to 100 ml and extracted with 3 portions of II (total 25 ml), dried with Na<sub>2</sub>SO<sub>4</sub> and made up to 25 ml. Iron and steel (< 200 mg) are decomposed with KClO<sub>4</sub> (0.1 g) and conc. HNO<sub>3</sub> (5 ml), heated with HCl (5 ml) and the S is reduced as described above. K. SAITO

133. A micro-diffusion method for the determination of hydrogen sulphide. R. C. Bray (Chester Beatty Res. Inst., Fulham Rd., London). *Analyst.*, 1958, 83, 379-381.—A filter-paper moistened with 0.01 ml of an aq. soln. containing 10 g of Zn acetate dihydrate and 2.5 g of Na acetate trihydrate in 50 ml is held between two polyethylene tubes with rubber bands inside a 50-ml cylindrical bottle. Part of the long side of the bottle is depressed inwards so that when lying horizontally the groove forms a partition separating two soln. before reaction. The polyethylene tubes clamping the paper may be continued outwards through the stopper so that inert gas may be introduced when necessary. After mixing the two soln. and during the diffusion the bottle, lying horizontally, is rotated by means of rollers. With Na<sub>2</sub>S and a phosphate buffer soln. at pH 7, diffusion is complete in 10 min. To measure the H<sub>2</sub>S, the paper is dropped into a test-tube containing a soln. of *p*-amino-NN-dimethylaniline sulphate in 1.5% v/v H<sub>2</sub>SO<sub>4</sub>, the stopper is inserted immediately and momentarily removed for the addition of 0.5 ml of a soln. of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (2% in 1.5% v/v H<sub>2</sub>SO<sub>4</sub>). Within 10 min. the extinction of the blue liquid is measured at 675 mµ and referred to a calibration graph. The apparatus is suitable for determining enzymically produced H<sub>2</sub>S and is sensitive to 1 µg.

A. O. JONES

134. 4-Amino-4'-chlorodiphenyl as analytical reagent for sulphate. T. A. Bengtsson (Lab. of Anal. Chem., Univ. of Uppsala, Sweden). *Anal. Chim. Acta*, 1958, 18 (4), 353-359.—Because low and irregular results were obtained in the determination of sulphate with 4-amino-4'-chlorodiphenyl by the method of Belcher *et al.* (*cf. Brit. Abstr. C*, 1953, 504), the molar solubility and ionisation product of the amine and the molar solubility of the amine sulphate were re-determined, and the values found were  $23 \times 10^{-6}$ , 4.21, and  $325 \times 10^{-6}$ , respectively, all at 20°. This last value is about 10 times that previously reported, and corresponds to 31 µg of SO<sub>4</sub><sup>2-</sup> per ml. The possibility of errors at various stages of the procedure is discussed in the light of these results, and it is suggested that more experience is needed before deciding on its suitability for organic micro-analysis. It is suggested that the excess of HCl in the reagent soln. (0.05 M according to the procedure of Belcher *et al.*, *Analyst.*, 1956, 81, 4) could be reduced by one-half, and the test soln. neutralised beforehand, which would favour completion of pptn. by a factor of 2 or 3. Further increase of pH in the final soln. will lead to pptn. of the amine. R. E. ESSERY

135. Determination of sulphate by direct titration with lead nitrate with dithizone as indicator. G. N. Nechiporenko (Hydrochem. Inst., Acad. Sci., USSR). *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1958, (3), 359-361.—The optimum conditions



for titrating  $\text{SO}_4^{2-}$  with  $\text{Pb}(\text{NO}_3)_2$  soln. are given. With  $<500$  mg of  $\text{SO}_4^{2-}$  per litre, a vol. of 10 to 20 ml is mixed with 8 to 15 ml of acetone and 1 to 3 ml of 0.1 N HCl and titrated with 0.1 M  $\text{Pb}(\text{NO}_3)_2$  in the presence of a few drops of a saturated soln. of dithizone in acetone. With 25 to 500 mg per litre, 2 to 5 ml is mixed with 5 to 10 ml of acetone and 0.05 to 0.1 ml of 0.1 N HCl and titrated with 0.005 M  $\text{Pb}(\text{NO}_3)_2$  in a 2-ml burette. The concn. of Cl<sup>-</sup> must not exceed 7 times that of the  $\text{SO}_4^{2-}$  and the concn. of  $\text{Ca}^{2+}$  must not exceed half that of the  $\text{SO}_4^{2-}$ .

G. S. SMITH

**136. Electrometric determination of sulphate ions.**

D. E. Galkin. *Trudy Tomsk. Univ.*, 1957, **145**, 163-172; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,589.—A non-compensation potentiometric titration method for determining  $\text{SO}_4^{2-}$  with  $\text{Pb}(\text{NO}_3)_2$  soln. using a bimetallic system of electrodes in combination with the ferro-ferricyanide electrode is described. It is established that platinum, gold and tungsten electrodes may be used as indicator electrodes, and silver, graphite and calomel electrodes as comparison electrodes. The optimum ratio of  $\text{Fe}(\text{CN})_6^{4-}$  to  $\text{Fe}(\text{CN})_6^{3-}$  is 1:200. To the soln. to be analysed add 0.1 M  $\text{K}_3\text{Fe}(\text{CN})_6$  (1 ml), 0.005 M  $\text{K}_4\text{Fe}(\text{CN})_6$  (0.1 ml) and one and a half times the vol. of ethanol (96%) and titrate with 0.1 N  $\text{Pb}(\text{NO}_3)_2$  to zero e.m.f. The error of the determination is  $>0.7\%$  abs. as compared with the gravimetric method.

C. D. KOPKIN

**137. Determination of trace amounts of selenium in sulphuric acid. Colorimetric method using 3,3'-diaminobenzidine.** Taeko Danzuka and Keihei Ueno (Res. Lab., Daijindo & Co., Ltd., Kumamoto, Japan). *Anal. Chem.*, 1958, **30** (8), 1370-1371.—As little as 5 to 25  $\mu\text{g}$  of Se per gram of  $\text{H}_2\text{SO}_4$  can be determined by the procedure described. The selenium complex with 3,3'-diaminobenzidine is extracted into toluene, the extinction of the extract being measured at 420 m $\mu$  vs. a reagent blank. The calibration curve follows Beer's law up to 25  $\mu\text{g}$  of Se per 10 ml of toluene. Ammonium chloride is used to prevent pptn. of diaminobenzidine sulphate. The effects of ammonium chloride, sulphate concn. and time on colour development are discussed. Under optimum conditions, the error can be kept within  $\pm 2\%$  in the concn. range quoted. It is claimed that Se may be determined in sulphur by this method, if the sulphur is first oxidised to sulphate.

F. L. SELFE

**138. Colorimetric determination of selenium and tellurium in dusts obtained in the lead industry.** V. P. Gladyshev (Kazakh State Univ.). *Zavod. Lab.*, 1958, **24** (3), 275-278.—An application of the method of Jilek *et al.* (*Anal. Abstr.*, 1957, **4**, 2585) is described. After removal of Pb as  $\text{PbSO}_4$ , a preliminary separation of Se and Te is carried out by pptn. with  $\text{SnCl}_2$ . The ppt. is dissolved in HCl with  $\text{HNO}_3$ , and the colorimetric methods with thiourea are applied.

G. S. SMITH

**139. Amperometric titration of selenite with hypobromite.** G. S. Deshmukh, M. G. Bapat, E. Balkrishnan and M. C. Eshwar (Chemical Lab., Hindu Univ., Benares, India). *Naturwissenschaften*, 1958, **45** (6), 129.—Solutions of selenous acid or sodium selenite, of arsenous oxide, NaOBr and  $\text{NaHCO}_3$  were used as recommended by Kolthoff *et al.* (*Analyst*, 1953, **78**, 405). A rotating platinum micro-electrode and the S.C.E. were used as indicator and reference electrodes, respectively, and it

was found that  $\text{Se}^{\text{IV}}$  is smoothly oxidised to  $\text{Se}^{\text{VI}}$  by hypobromite according to the equation  $\text{NaOBr} + \text{SeO}_3^{2-} = \text{NaBr} + \text{SeO}_4^{2-}$ .

E. KAWERAU

**140. Separation of tellurite and tellurate by ion exchange.** Kenjiro Kimura, Nagao Ikeda and Mariko Inarida (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *Japan Analyst*, 1958, **7** (3), 174-176.—Whereas  $\text{TeO}_3^{2-}$  ( $\approx 10$  mg) are adsorbed on Amberlite IRA-400 (Cl) (100 mesh) (column diameter 12 mm, height 5 cm) from 3 to 12 N HCl soln.,  $\text{TeO}_4^{2-}$  ( $\approx 10$  mg) in 2 to 12 N HCl pass through the column. This behaviour holds even for tracer-scale concn. and can be used for the separation of Te in different valency states in fission products.

K. SAITO

**141. Coulometric determination of chromium.** L. Meites (Dept. of Chem., Polytech. Inst. of Brooklyn, N.Y., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (4), 364-372.—The analysis, with apparatus and procedure previously described (*cf. Anal. Abstr.*, 1955, **2**, 3551), is based on controlled potential electrolysis of the sample in 6 M HCl at a large stirred mercury cathode maintained at  $-1.10$  V vs. the S.C.E. This reduces the  $\text{Cr}^{\text{III}}$  to  $\text{Cr}^{\text{II}}$ . Of possible interfering metals, Cd, Cu, Pb, In, Tl, Sn and Zn are reduced to their amalgams, and can be removed by draining off the mercury and replacing it with fresh. Uranium is then re-oxidised to non-interfering  $\text{U}^{4+}$  by a controlled potential electrolysis at  $-0.80$  V vs. the S.C.E., and the  $\text{Cr}^{\text{II}}$  is then re-oxidised to  $\text{Cr}^{\text{III}}$  at  $-0.40$  V vs. the S.C.E., the current consumed in this oxidation being measured. Tungsten should previously be removed by a double dehydration with HCl and cinchonine since enough enters solution in 6 M HCl to cause slight current consumption. Selenium, Te and Re would interfere, but are rarely present in significant amounts. Vanadium is measured with the Cr, and must be determined separately and allowed for. Molybdenum interferes when present in large amounts, but can be corrected for if data on known mixtures are collected. Results for standard alloys containing from 0.23 to 19.12% of Cr showed errors ranging from  $-0.26$  to  $+0.5\%$  of Cr.

R. E. ESSERY

**142. Amperometric determination of chromium, vanadium and manganese in titanium alloys.** T. V. Araf'eva and R. G. Pats. *Sb. Nauch. Trud., Gos. Nauch. Inst. Tsvet. Met.*, 1958, (14), 74-79; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,430.—To determine Cr, V and Mn in titanium alloys, use is made of the previously described amperometric method for their determination in light-alloy steels (Butenko and Bekleshova, *Zavod. Lab.*, 1950, **16**, 6, 650), based on the successive titration with ferrous soln. of total Cr, V and Mn [after oxidation with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in the presence of  $\text{AgNO}_3$  to  $\text{CrO}_4^{2-}$ ,  $\text{VO}_4^{3-}$  and  $\text{MnO}_4^-$ ], total Cr and V (after destroying  $\text{MnO}_4^-$  with NaCl), and V alone (after oxidation with  $\text{KMnO}_4$ ). It is established that, in the titration of V, more reliable results are obtained if  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$  instead of oxalic acid is used to destroy excess of  $\text{KMnO}_4$ . The presence of a 200-fold amount of Ti does not cause interference in the amperometric determination of Cr, V and Mn; to avoid hydrolysis of Ti, the acidity of the soln. being titrated should be  $<10\%$  by vol. There is no interference from Mo or Al.

C. D. KOPKIN

**143. Decomposition and analysis of chromic oxide.** V. G. Scherbakov and R. M. Veitsman (All-Union Sci. Res. Inst. of Hard Alloys). *Zavod. Lab.*, 1958,



**24 (3), 280-281.**—For dissolution of  $\text{Cr}_2\text{O}_3$ , the most effective and rapid method is heating with conc.  $\text{H}_2\text{SO}_4$  in the presence of  $\text{K}_2\text{Cr}_2\text{O}_7$ . To determine the content of  $\text{Cr}_2\text{O}_3$  in technical chromic oxide, the sample (0.2 g) is heated with continuous stirring with 10 ml of 0.1 N  $\text{K}_2\text{Cr}_2\text{O}_7$  and 10 ml of conc.  $\text{H}_2\text{SO}_4$  until the liquid becomes clear and then for another 0.5 to 1 min. The cooled soln. is mixed first with 50 ml of water and then with 65 to 70 ml of 24%  $\text{NaOH}$  soln., added in small portions, followed by 40 ml of 2.5%  $\text{H}_2\text{O}_2$  soln. After being boiled for 5 min. and then cooled, the soln. is treated with 65 to 70 ml of 27%  $\text{H}_2\text{SO}_4$ , 5 ml of  $\text{H}_3\text{PO}_4$  (sp. gr. 1.7) and 1 ml of a 0.1% soln. of sodium or barium diphenylaminesulphonate and titrated with a standard soln. of  $\text{Fe}^{II}$ . G. S. SMITH

**144. Determination of chromic oxide, total iron and ferrous oxide in chrome ores and chromomagnesian refractory materials.** E. G. Kondrachina and O. A. Songina. *Trudy Inst. Stroit. i Stroimaterial., Akad. Nauk KazSSR*, 1958, **1**, 149-159; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,457.—An amperometric method is used after decomposition of the samples by treatment with a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  or by a rapid fusion with  $\text{Na}_2\text{O}_2$  with a protective layer of  $\text{Na}_2\text{CO}_3$ . Treat 0.2 to 0.25 g of ore (or 0.5 g of chromomagnesian brick) with 20 to 25 ml of a mixture (2:1 or 1:2) of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) and  $\text{H}_3\text{PO}_4$  (sp. gr. 1.7) in a closed heat-resistant beaker while warming and stirring to complete decomposition of the sample, and make up to 200 or 250 ml. To determine  $\text{Cr}_2\text{O}_3$ , add to 50 ml of the resulting soln.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (to oxidise  $\text{Cr}^{3+}$  to  $\text{Cr}_2\text{O}_7^{2-}$ ), boil (to decompose excess of oxidant), add a few drops of  $\text{HCl}$  (to reduce  $\text{MnO}_4^-$ ), again boil, make up to 200 or 250 ml, and titrate 20 ml of the resulting soln. with 0.1 N  $(\text{NH}_4)_2\text{SO}_4\text{-FeSO}_4$  at +1 V with a rotating platinum electrode and a mercury iodide half-cell. To determine  $\text{Fe}_2\text{O}_3$ , add to 25 ml of the original soln. aluminium ribbon (to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ ), warm, cool, stir for 3 min. (to oxidise  $\text{Cr}^{3+}$  and  $\text{Ti}^{3+}$ ) and titrate amperometrically with 0.1 N or 0.05 N  $\text{K}_2\text{Cr}_2\text{O}_7$ . To determine  $\text{FeO}$  use Shein's modified vanadometric method (*Zavod. Lab.*, 1937, **6**, 10) with amperometric determination of the end-point of the titration instead of the indicator method (*cf.* Kondrachina *et al.*, *Anal. Abstr.*, 1958, **5**, 3709).

C. D. KOPKIN

**145. Extraction of the chloride complexes of molybdenum and tungsten in the presence of phosphoric acid.** F. G. Zharovskii. *Ukr. Khim. Zhur.*, 1957, **23** (6), 767-770; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,365.—The extraction of W and Mo as the chloride complexes with diethyl ether was studied. It is established that W is extracted by ether only at a concn. of  $\text{HCl}$   $\leq 8$  N. The partition coeff. ( $k$ ) of W between ether and  $\text{HCl}$  is a maximum at a concn. of  $\text{HCl}$  of 8 N. At higher concn.  $k$  decreases, and at lower concn. there is separation of tungstic acid, which collects at the phase interface and contaminates both phases. With an increase in the concn. of W,  $k$  decreases. The value of  $k$  for Mo is maximum at a concn. of  $\text{HCl}$  of  $\approx 6$  N. To hold W in the aq. phase under the optimum conditions for the extraction of Mo (6 N  $\text{HCl}$ ), the extraction is carried out in the presence of 0.4 N  $\text{H}_3\text{PO}_4$ . A single extraction with an equal volume of ether then extracts  $\approx 76\%$  of the Mo; W remains completely in the aq. phase. Oxalic acid and  $\text{HF}$  show an analogous effect on the extraction of W; however, being stronger complexing reagents for

Mo and W than  $\text{H}_3\text{PO}_4$ , they hold in the aq. phase not only W but also Mo. C. D. KOPKIN

**146. Determination of tungsten in titanium, zirconium and their alloys.** D. F. Wood and R. T. Clark (Res. Dept., I.C.I. Ltd., Metals Div., Kynoch Works, Wotton, Birmingham, England). *Analyst*, 1958, **83**, 326-334.—For the determination of W in titanium and its alloys two absorptiometric procedures have been developed. In the thiocyanate method, an aliquot of the soln. of the sample (0.2 g) in  $\text{HCl}$  and fluoroboric acid is treated with  $\text{HCl}$  and  $\text{NH}_4\text{SCN}$  soln., then adjusted to a known vol., set aside for 5 min. at  $20^\circ \pm 1^\circ$  and the extinction is measured at 400  $m\mu$  and referred to a calibration graph. With slight modification the method is extended to the determination of W in zirconium and its alloys. For the development of the thiocyanate colour,  $\text{HCl}$  containing dissolved titanium is added before addition of the  $\text{NH}_4\text{SCN}$ . In the second method, the sample (titanium or zirconium) is dissolved in dil.  $\text{H}_2\text{SO}_4$  and fluoroboric acid, the soln. is oxidised with a little  $\text{HNO}_3$ , and nitrous fumes are removed by boiling. To an aliquot portion is added a soln. of iron in dil.  $\text{H}_2\text{SO}_4$ , the soln. is evaporated to fuming-point, cooled, treated with  $\text{SnCl}_2$  and warmed with a soln. of diethyl in isoamyl acetate. The organic layer is separated and washed, and its extinction is measured at 630  $m\mu$  and referred to a calibration graph.

A. O. JONES

**147. Determination of uranium with cupferron in the presence of ammonium ethylenediaminetetraacetate.** B. Bieber and Z. Večera (Res. Inst. Materials and Technol., Brno, Czechoslovakia). *Chem. Listy*, 1958, **52** (3), 439-443.—Salts of  $\text{U}^{VI}$  can be determined gravimetrically by pptn. with aq. cupferron soln. in neutral soln. The crystalline ppt. can be isolated and ignited to  $\text{U}_3\text{O}_8$ . Numerous elements can be masked with EDTA (ammonium salt) (I) or with tartaric acid. Only Be, an excess of Ti or Zr, and fluorides and carbonates interfere. *Procedure for ores and concentrates*—Weigh the finely powdered ore (0.1 to 1 g) into a 400-ml vessel, decompose by boiling with conc.  $\text{HNO}_3$  (20 ml), add conc.  $\text{H}_2\text{SO}_4$  (10 ml) and evaporate on a sand bath. Cool, dilute with  $\text{H}_2\text{O}$ , and filter off  $\text{SiO}_2$ ,  $\text{CaSO}_4$  and  $\text{PbSO}_4$ . Add an excess of I soln. to the filtrate, adjust to a pH of 7 to 8 with aq.  $\text{NH}_3$  and precipitate with an aq. soln. of cupferron (2%). Filter off the ppt. on a paper filter, wash with cupferron soln. (0.2%) containing I, dry the ppt. and ignite in an electric furnace at  $800^\circ$  to  $1000^\circ$ . In the presence of a large amount of Ti or Zr dissolve the ppt. in a mixture of conc.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (1:2), evaporate and remove Ti and Zn by pptg. with cupferron in  $\text{H}_2\text{SO}_4$  soln. (10%), and determine U in the filtrate in neutral medium as described above. J. ŽYKA

**148. A difference photometric method for determining uranium in perchloric acid medium.** T. W. Steele (Gov. Metallurgical Lab., Univ. of the Witwatersrand, Johannesburg, S. Africa). *Analyst*, 1958, **83**, 414-421.—The sample (2 g) is ignited at  $950^\circ$  for 2 hr. in a porcelain dish. The dish is then placed in a covered beaker and heated with 70 to 72%  $\text{HClO}_4$  (15 ml) till the water has been expelled and the liquid is then boiled for 5 min. The dish is washed and removed, the liquid is evaporated to fuming-point, boiled, cooled, diluted with water ( $\approx 20$  ml), boiled and filtered through Whatman No. 3 paper, the paper and residue being washed

with 0.2%  $\text{HClO}_4$ . The filtrate is evaporated to  $\approx 35$  ml ( $< 30$  ml), cooled and adjusted to slightly less than 50 ml, placed near the spectrophotometer together with a supply of diluting water and the standard soln. of U and, after  $< 3$  hr., the final adjustment of vol. is made. The extinction of the soln. is measured against a series of standard soln. at 420 m $\mu$ . To avoid errors due to temp. variations, the procedure for filling and inserting the cells is standardised. Marked interference occurs with  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ , Au, V, Ni, Co and Fe. The amounts of these that give a 0.1% error with a 2-g sample are quoted.

A. O. JONES

**149. Paper-chromatographic analysis of irradiated uranium in a hydrofluoric acid medium.** C. E. Crouthamel and A. J. Fudge (Argonne Nat. Lab., Lemont, Illinois). *J. Inorg. Nuclear Chem.*, 1958, **5** (3), 240-244.—After dissolution of neutron-irradiated  $\text{U}_3\text{O}_8$  in  $\text{HNO}_3$  and the replacement of the  $\text{HNO}_3$  by HF, the mixture was developed on Whatman 3-MM, No. 1, or No. 2 paper strips by using an HF-ethyl methyl ketone solvent (20 g or 60 g of 49% HF per 100 ml of ethyl methyl ketone) or 49% HF alone; the atmosphere in the developing vessel was saturated with the solvent. The  $R_F$  values for 20 elements are tabulated.

G. J. HUNTER

**150. Determination of uranyl nitrate in the presence of nitric acid by acidimetric titration.** J. Čepelák, J. Malý and V. Veselý (Inst. Nucl. Physics, Prague). *Chem. Listy*, 1958, **52** (3), 547-549.—Nitric acid liberated by the reaction of uranyl nitrate with  $\text{H}_2\text{O}_2$  can be titrated visually or potentiometrically. *Potentiometric titration*—To the soln. containing uranyl nitrate in the presence of  $\text{HNO}_3$  add  $\text{H}_2\text{O}_2$  (30%) (5 ml) and titrate with 0.1 N NaOH. Carry out a second titration without the addition of  $\text{H}_2\text{O}_2$  and calculate the  $\text{HNO}_3$  by difference. *Visual titration*—To the sample containing 1 to 2.5 g of uranyl nitrate in 100 ml in the presence of free  $\text{HNO}_3$  add  $\text{H}_2\text{O}_2$  (30%) (5 ml) and Tashiro indicator (10 drops) and titrate with 0.1 N NaOH till the violet colour changes to yellow-green. Titrate the free  $\text{HNO}_3$  in another sample with the use of a mixed indicator (70 ml of 0.1% dimethyl yellow in ethanol and 30 ml of 0.1% aq. methylene blue soln.) (6 to 8 drops); the colour change is wine red to green. In a soln. of pH 2 to 5 the procedure described gives quant. results, with an average error of  $\pm 2\%$ .

J. ZÝKA

**151. Extraction of uranyl nitrate from the system water-nitric acid-ammonium nitrate with diethyl ether.** J. Čepelák, J. Malý and V. Macháček (Inst. Nucl. Physics, Acad. Sci., Prague). *Chem. Listy*, 1957, **51** (12), 2195-2199.—The equilibrium distribution of  $\text{UO}_2(\text{NO}_3)_2$  between aq.  $\text{HNO}_3$  and diethyl ether in the presence of  $\text{NH}_4\text{NO}_3$  has been studied. The distribution between the phases is different for N and 5 N  $\text{HNO}_3$ . Absorption spectra of both phases and m.p. curves of the aq. phase show that, under equilibrium conditions with 5 N  $\text{HNO}_3$ , U is present in the aq. phase as  $\text{UO}_2^{2+}$  and as the complex ion  $\text{UO}_2(\text{NO}_3)_2^-$  in the org. phase.

J. ZÝKA

**152. Determination of the oxidation state of uranium in apatite and phosphorite deposits.** R. S. Clarke, jun., and Z. S. Altschuler (U.S. Geol. Survey, Washington 25, D.C.). *Geochim. et Cosmochim. Acta*, 1958, **13** (2-3), 127-142.—An

analytical procedure was developed for the determination of U in apatite. *Procedure*—Dissolve 0.1 g of finely powdered carbonate-fluorapatite in 1.5 M  $\text{H}_3\text{PO}_4$  (50 ml) at 5° or, for more highly crystalline fluorapatite, 1.2 M HCl containing 1.5% of hydroxylamine hydrochloride (100 ml) at 5°. Filter the cold soln. through a glass-fibre filter-paper in a Gooch crucible, and add a cold soln. (3 ml) of 1.0 mg of Ti per ml in 10%  $\text{H}_2\text{SO}_4$ , followed by cold aq. 6% cupferron soln. Keep cold for 10 to 15 min., filter, and wash ( $\times 8$ ) with a cool soln. of 6% HCl and 0.15% cupferron; ignite the paper and ppt. in platinum. Dissolve the ignited residue in  $\text{K}_2\text{S}_2\text{O}_8$  soln. or in HF- $\text{HNO}_3$ , taking up the residue in 7% (v/v)  $\text{HNO}_3$ ; add an aliquot (5 ml) of this soln. to a test-tube containing  $\text{Al}(\text{NO}_3)_3$  (9.5 g) of low U content. The U is then determined by a standard ethyl acetate extraction-fluorimetric procedure (Grimaldi et al., *U.S. Geol. Surv. Circ.*, 1952, 199). The validity and limitations of the method have been determined by spike experiments.

R. A. HOWIE

**153. New method for the determination of uranium in phosphates, coal ash, bauxite, etc., by means of ion exchange.** J. Korkisch, A. Farag and F. Hecht (Chem. Inst., Univ., Wien). *Z. anal. Chem.*, 1958, **161** (2), 92-100.—A column of strongly basic ion-exchange resin (Cl<sup>-</sup> form) retains U from 4 N HCl containing ascorbic acid. The U subsequently eluted with N HCl can be determined by polarography or by u.v. fluorescence. There is interference from  $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$ ,  $\text{Sn}^{4+}$  and  $\text{NO}_3^-$ . For polarography, a portion of the eluate containing 0.1 to 10  $\mu\text{g}$  of U is evaporated to dryness and ignited, dissolved in 4 N HCl and again evaporated. The residue is dissolved in 0.01 N  $\text{HNO}_3$  and the U determined polarographically. For the fluorimetric determination, the eluate is evaporated and heated for 20 min. at 640° with a melt comprising  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and NaF in the ratio 9:9:2. After cooling, the melt is kept in a desiccator overnight and the fluorescence under u.v. light is measured with the top surface facing the photocell. The procedure has been applied to a variety of phosphates, silicate rocks, bauxites and coal ash.

G. BURGER

**154. Analysis of Italian uraniferous minerals. II. Separation from acid and basic lyes of the uranium contained in an autinitic Piedmontese rock.** M. Lucco Borlera (Turin Polytechnic, Italy). *Ric. Sci.*, 1958, **28** (3), 523-532.—The most satisfactory procedure for the pptn. of U from the sulphuric extract from an autinitic (lime uranite) rock was pptn. as uranous pyrophosphate. The optimum conditions for reduction of the  $\text{U}^{6+}$  (with Fe) and the acidity for pptn. have been determined, in order to minimise the simultaneous pptn. of ferric pyrophosphate. Losses of U occurred if pptn. was carried out with  $\text{Na}_2\text{HPO}_4$ . The best conditions for alkali treatment of the mineral (concn. of  $\text{Na}_2\text{CO}_3$ - $\text{NaHCO}_3$ , time and temp. of treatment), followed by pptn. of the U as sodium uranate, have also been examined, for the avoidance of the simultaneous extraction of  $\text{SiO}_2$ , and the loss of U by pptn. as phosphate.

L. A. O'NEILL

**155. Separation of uranium from thorium by means of ion exchange and the fluorimetric determination of uranium.** E. Tomic, I.-M. Ladenbauer and M. Pollak (Chem. Inst., Univ., Wien). *Z. anal. Chem.*, 1958, **161** (1), 28-38.—A column of strongly basic ion-exchange resin (Cl<sup>-</sup> form) retains

U from a 0.5 N HCl soln. while Th passes through. The U can be eluted with N HCl. The eluate is evaporated to dryness and the residue is heated for 20 min. to a constant ( $\pm 10^\circ$ ) temp. between  $610^\circ$  and  $650^\circ$  with 5 g of a melt containing  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and NaF in the proportion 9:9:2. The fluorescence under u.v. can be measured by means of a cheap and simple apparatus comprising a mercury vapour lamp, photocell and galvanometer. The U can be determined with a mean error of 6.4% (range -2% to +20%, 10 determinations) by comparison of the galvanometer reading with a calibration curve. Ions that interfere by quenching include those of Cr, Mn, Co, Ni, Ag, La, Pt, Au, Pb, Ce, Pr and Nd (1 to 10  $\mu\text{g}$ ); Fe, Cu, Zn, Sn and Th (10 to 50  $\mu\text{g}$ ); Ti and W (50 to 1000  $\mu\text{g}$ ). The amounts after each group represent those causing 10% or more reduction in emission. The sample should contain  $> 5 \text{ mg}$  of U. By a polarographic method a few tenths of a  $\mu\text{g}$  of U can be determined. The Th (1 to 60  $\mu\text{g}$ ) can be determined photometrically by means of quercetin. G. BURGER

**156. Spectrographic analysis by evaporation. V. Analysis of plutonium by evaporation in a vacuum.** A. N. Zaidel', N. I. Kaliteevskii, L. V. Lipis and V. M. Tarakanov (A. A. Zhdanov State Univ., Leningrad). *Optika i Spektroskopiya*, 1957, **3** (1), 16-20; *Ref. Zhur., Khim.*, 1958, Abstr. No. 14,222.—Evaporation in a vacuum is used to determine traces of impurity in plutonium. It is established experimentally that the max. temp. for the evaporation of impurities from  $\text{PuO}_2$  is  $1800^\circ$  and that the time should be 2 min. Because of the toxicity and high cost of Pu, the standards are prepared on a basis of  $\text{ThO}_2$ ; the feasibility of such replacement for a semi-qual. analysis has been satisfactorily proved. Standards for the determination of Na, K, Li, Mn, Si, B, Co, Cd, Ag, Be, Ba and Ni are prepared by grinding in agate mortars or platinum dishes. Samples of metallic Pu are converted into  $\text{PuO}_2$  by slow heating (to prevent combustion) in a muffle-furnace. The samples and standards are weighed into graphite crucibles and placed in the vacuum evaporation apparatus in a shielded room. The spectra are excited with copper electrodes. The accuracy and sensitivity of the analysis is not less than in the analysis of other metals (Th, U, Zr, Be). (See also *Anal. Abstr.*, 1958, **5**, 743.)

C. D. KOPKIN

**157. The co-precipitation of small amounts of plutonium on lanthanum fluoride in the presence of uranium.** G. N. Walton, E. Furby and V. Owen (A.E.R.E., Harwell, England). A.E.R.E. Report C/R 2388, 1958, 24 pp.—The extraneous  $\alpha$ -activity carried down during the determination of small amounts of Pu (<500 c.p.m. per ml) is caused by adsorption of microgram amounts of  $\text{UO}_2^{2+}$  by the  $\text{LaF}_3$  ppt. in such a way that they cannot be easily washed off. The percentage adsorbed increases with decreasing concn. of  $\text{UO}_2^{2+}$ . The importance of this effect is discussed for the use of  $\text{LaF}_3$  when determining (i) very small amounts of Pu in uranium soln. or of U in plutonium soln., and (ii) trace amounts of  $\text{Pu}^{\text{VI}}$  in the presence of  $\text{Pu}^{\text{III}}$  and  $\text{Pu}^{\text{IV}}$  by the "holding oxidant" method (McVey *et al.*, A.E.R.E. Reports CN 1588 and 3678), or when separating the transuranic elements (Np, Am, Cm). In none of these instances is the present technique of co-pptn. with  $\text{LaF}_3$  considered suitable. Pending the development of a more satisfactory method (preferential selection of Pu by solvent

extraction or kick-sorting of  $\alpha$ -pulses), the adsorption effects can be minimised by using smaller concn. of  $\text{La}(\text{NO}_3)_3$  (but  $< 50 \mu\text{g}$  of La). If the "holding oxidant" method is used, addition of  $\text{UO}_2^{2+}$  as a "hold-back" carrier for Pu is necessary. This method is not valid for amounts of Pu comparable in activity to that of microgram amounts of U.

W. J. BAKER

**158. Radiochemical determination of neptunium-239 and plutonium-239 in homogeneous reactor fuel and blanket solutions.** F. L. Moore (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1368-1369.—The method is based on the carrying of the two isotopes by lanthanum fluoride, followed by liquid-liquid extraction of the  $^{239}\text{Np}$  with 2-thenoyltrifluoroacetone-xylene. The isotopes are recovered with a precision of  $99 \pm 3\%$ .

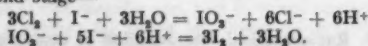
K. A. PROCTOR

**159. Photometric determination of fluorine in zinc concentrates and electrolytes as the thorium-alizarin lake.** S. D. Gur'ev and V. P. Ioffe. *Sb. Nauch. Trud., Gos. Nauch. Inst. Tsvet. Met.*, 1958, (14), 61-66; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,419.—The method described is based on the decolorisation by  $\text{F}^-$  of the red compound of Th with alizarin red S. It is established that the max. light absorption of the coloured soln. is at 530  $\text{m}\mu$ ; the colour is stable for 4 hr. To determine F in zinc concentrates, fuse 0.5 to 1 g of sample in an iron crucible with 3 to 5 g of  $\text{Na}_2\text{O}_2$ , extract the melt with water (20 to 30 ml), transfer the soln. and residue to a distillation flask, add 0.1 or 0.2 g of quartz or ferrosilicon and a few drops of phenolphthalein, and close the flask with a cork containing a thermometer and a dropping-funnel. Add dil.  $\text{H}_2\text{SO}_4$  (1:1), with cooling, till the soln. is colourless, and then conc.  $\text{H}_2\text{SO}_4$  until the soln. is 50% in  $\text{H}_2\text{SO}_4$ . Attach a vertical condenser to the side arm of the flask and heat at  $140^\circ$  to  $160^\circ$  till 100 ml of distillate is obtained. Neutralise this with 0.1 N NaOH to phenolphthalein, evaporate to 20 or 40 ml, filter and make up to a known vol. Dilute a 1 to 5-ml aliquot to 30 or 40 ml, add 5 ml of a soln. of alizarin red S (0.092 g per litre) and one drop of 0.3 N  $\text{HNO}_3$ , make up to 50 ml, mix, add 5 ml of thorium reagent [11 g of  $\text{Na}_2\text{SO}_4$ , 22.5 ml of 85% formic acid, 52 g of Na formate and 0.26 g of  $\text{Th}(\text{NO}_3)_4$  in 500 ml; pH 3-5], mix, and after 30 min. measure the extinction in a 50-mm cell with a green filter, against a control blank. To determine F in electrolytes, place 50 ml of the soln. in a distillation flask and continue as described above. Reproducible results are obtained.

C. D. KOPKIN

**160. Catechol - ferric complexes and their application in fluoride determination.** Shu-Chuan Liang and Yung-Chao Chen (Inst. of Chem., Acad. Sinica). *Acta Chim. Sinica*, 1958, **24** (1), 79-86.—Complex formation between  $\text{Fe}^{3+}$  and catechol in the pH range 2 to 12 was investigated spectrophotometrically between 400 and 800  $\text{m}\mu$ . In addition to the 3 complexes previously reported, 2 new ones are identified. These are greenish yellow, green, blue, violet and red at pH 2, 3.5 to 5.1, 5.86, 8.2 to 8.7, and 9 to 10.2, respectively. Fluoride bleaches the colour formed in soln. containing  $\text{Fe}^{3+}$  and catechol at pH 2 to 4, but not at pH 4.2 to 10. The colour of the  $\text{Fe}^{3+}$ -catechol complex is not very stable and the sensitivity of the test for  $\text{F}^-$  based on this reagent is lower than that with ferron - ferric or resacetophenone - ferric reagents. S. H. YUEN

**161. Conductimetric determination of chlorine by titration with potassium iodide.** D. Ceausescu (Inst. of Hygiene, Timisoara, Romania). *Stud. Cercet. Chim., Cluj*, 1957, **8** (3-4), 281-284.—The method is based on the two stages of the reaction of Cl with KI, in which there is an increase of  $H^+$  in the first stage followed by their removal as  $H_2O$  in the second stage—



The angle formed by the two branches of the titration curve is sharp, and shows the end-point clearly. H. SHER

**162. Mercurimetry for the determination of chloride.** E. Dannenberg (Hosp. Mixto, Santiago del Estero, Argentina). *Anal. Chim. Acta*, 1958, **18** (4), 315-316 (in German).—Chlorides in acid soln. can be titrated with  $Hg(NO_3)_2$  soln. as accurately as with  $AgNO_3$ , with 0.5% ethanolic diphenylcarbazone as indicator. To 250 ml of the soln. to be examined add 10 drops of indicator and, if necessary, 1 to 3 drops of conc.  $HNO_3$ , and titrate with 0.1 N  $Hg(NO_3)_2$  to a rose-violet end-point; this is sharp, since an 0.05-ml excess of titrant gives a clear violet coloration. The titrant is prepared by dissolving 10.83 g of  $HgO$  in 3 to 4 ml of conc.  $HNO_3$  and diluting to 1 litre. The clear soln. obtained is stable to light. The indicator soln. is stable for at least 4 months. All colourless chlorides can be titrated, and the proportion of acid present is not critical. Cupric chloride can be titrated, but not  $FeCl_3$ . Phosphates and carbonates do not interfere. The method is convenient and satisfactory for the standardisation of pure HCl soln., and is much cheaper than those in which Ag is used. R. E. ESSERY

**163. Amperometric determination of chloride in copper and zinc sulphate solutions.** O. A. Songina (Kazakh State Univ.). *Zavod. Lab.*, 1958, **24** (3), 273-275.—The normal amperometric titration of  $Cl^-$  with a platinum electrode is unsatisfactory when Cu is present because Cu tends to deposit on the electrode and this is followed by deposition of some of the Ag from the titrant. A satisfactory method is to apply a potential to the platinum electrode of +0.4 V vs. a mercurous iodide reference electrode. No Cu is deposited and a further advantage is that dissolved O is not reduced. G. S. SMITH

**164. Analysis of mixtures of chlorides and bromides.** I. Ubaldini and F. Capizzi Maitan (Inst. Chem. Ind., Polytech., Milan). *Ann. Chim., Roma*, 1958, **48** (3), 209-217.—When one halide is not present in considerable excess, the total halide may be determined argentimetrically;  $Br^-$  are then oxidised to  $Br_2$  by means of  $KBrO_3-H_2SO_4$  and the  $Cl^-$  are determined by difference. When  $Cl^-$  are present in a large excess, they may be determined directly as  $AgCl$  and the silver salt of 2-mercaptobenzothiazole. If present in small amount, the  $Cl^-$  are concentrated by passage over an anion-exchange resin (sulphate form). The  $Cl^-$  and  $Br^-$  may be pptd. as their silver salts, dissolved in aq.  $NH_3$ , freed from Ag by passage through a cation-exchange resin ( $NH_4^+$  form) and one of the halides eliminated by passage through an anionic-exchange resin in the form of the other halide. A. G. COOPER

**165. Identification and determination of chlorites in the presence of chlorates.** G. R. Levi and E. Res Garrini (Ist. di Chim. Gen., Univ., Pavia, Italy).

*Gazz. Chim. Ital.*, 1957, **87**, 7-10.—Specific analytical tests for  $ClO_3^-$  in the presence of  $ClO_2^-$  depend on the reduction of  $ClO_3^-$  to  $Cl^-$  by certain heavy-metal hydroxides. Of the metal hydroxides examined, only those of Ni and Co are applicable; the others catalyse the disproportionation of  $ClO_3^-$ . Procedure—For the detection of  $ClO_3^-$ , a micro drop of  $NiSO_4$  soln. containing  $\approx 60 \mu g$  of  $Ni^{2+}$  is mixed with a micro drop of NaOH soln. containing  $\approx 200 \mu g$ , and then a micro drop of the test soln. is added. The soln. is covered and heated on a water bath ( $40^\circ$  to  $50^\circ$ ) for a few minutes. In the presence of  $ClO_3^-$ , black specks or a black coloration develop in the green mass. The test has a sensitivity of  $1 \mu g$  of  $ClO_3^-$ , and is valid in the presence of  $BrO_3^-$ ,  $IO_3^-$ ,  $IO_4^-$  and  $ClO_2^-$ . For the determination of  $ClO_3^-$ , a ppt. of  $Co(OH)_2$  is prepared by treating  $M CoSO_4$  with a 1% excess of 2 N NaOH. The test soln. is added and the mixture is placed on a boiling-water bath for 2 hr. The soln. is cooled and transferred to a standard flask, and a suitable aliquot is removed through a dry filter; the  $Cl^-$  are then titrated. J. H. WATON

**166. Quantitative determination of chlorates and bromates.** O. A. Sosnovtseva and M. N. Vladimirova *Sb. Nauch. Trud. Kulbyshevsk. Ind. Inst.*, 1957, (7), 67-72; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,390.—The reducing action of  $As_2O_3$ ,  $Fe^{2+}$ ,  $NO_2^-$ ,  $Sn^{2+}$ ,  $Sb^{3+}$  and oxalate on  $ClO_3^-$  and  $BrO_3^-$  is studied. It is established that all the reducing agents indicated, with the exception of oxalate, react with both chlorates and bromates; oxalate shows no reducing action on  $ClO_3^-$ . A new method evolved for the determination of  $ClO_3^-$  and  $BrO_3^-$  when present together is based on the differing action of reducing agents. Dissolve the sample (0.5 to 0.6 g) in water and make up to 250 ml. To determine  $BrO_3^-$ , add to 10 ml of the soln. N oxalic acid (2 ml) and 0.5 N  $HNO_3$  or  $H_2SO_4$  (10 ml), dilute with water, boil for 3 or 5 min., cool, add 5 ml of standard 0.1 N  $AgNO_3$  and titrate excess of  $AgNO_3$  with 0.05 N  $NH_4SCN$ . To determine total  $ClO_3^-$  plus  $BrO_3^-$ , add to 25 ml of the original soln. 5 ml of 0.1 N  $NaNO_2$  as reducing agent and 15 ml of 0.5 N  $HNO_3$ ; boil for 5 to 7 min., cool, add 4 drops of  $HNO_3$  (sp. gr. 1.4), 4 drops of a 50% soln. of  $Fe(NO_3)_3$  and 4 drops of a 15% soln. of  $NH_4SCN$  and titrate with 0.1 N  $Hg_2(NO_3)_2$  till the soln. is completely colourless. Carry out a blank titration simultaneously by adding 4 ml each of  $HNO_3$  and the soln. of  $Fe(NO_3)_3$  and  $NH_4SCN$  to 50 ml of water and titrating with 0.1 N  $Hg_2(NO_3)_2$  till the soln. is colourless. Chlorate is determined by difference. C. D. KOPKIN

**167. Separation of manganese as its diethyldithiocarbamate complex in the presence of cerium, and its determination.** J. Clinch and M. J. Guy (Anal. Lab., Thorium Ltd., Ilford, Essex, England). *Analyst*, 1958, **83**, 429-431.—The sample soln. (containing  $\approx 100 \mu g$  of Mn) with a few drops of cresol red indicator is treated with aq.  $NH_3$  till the colour of the indicator just changes to purple (pH 7.5 to 8.0), and the diluted liquid is well shaken and extracted ( $3 \times 10$  ml) with diethylammonium diethyldithiocarbamate in  $CHCl_3$ . The combined extracts are evaporated with 5 ml of 10 N  $H_2SO_4$  until the  $CHCl_3$  has been removed, and after addition of  $HNO_3$  the liquid is heated to fuming. To the partly cooled residue are added 5 ml of dil.  $H_3PO_4$  (1 + 4), 10 ml of water and  $\approx 0.2$  g of  $KIO_4$  and the soln. is boiled for 5 min. or until a pink colour appears, kept hot for 10 min. and then cooled and



diluted to 25 ml. The extinction is then measured absorptiometrically. Cyanide (1 g of KCN) interferes over the whole pH range at which extraction takes place,  $\text{NaH}_2\text{PO}_4$  does not interfere, but pyrophosphate reduces the recovery of 100  $\mu\text{g}$  of Mn to 16  $\mu\text{g}$ . Hydroxylamine (1 g) and  $\text{SO}_2$  (1 g of  $\text{Na}_2\text{S}_2\text{O}_3$ ) cause little interference, reducing the recovery of 100  $\mu\text{g}$  to 94  $\mu\text{g}$ . A. O. JONES

**168. Activation analysis of manganese in ferromanganese alloy using radium-beryllium neutron source.** Yuzuru Kusaka (Dept. of Chem., Fac. of Sci., Konan Univ., Higashinada-Ku, Kobe). *Bull. Chem. Soc. Japan*, 1958, **31** (2), 216-219 (in English).—A 50-mg Ra-Be source with a thermal neutron flux of about  $10^8$  to  $10^9$  neutrons per sq. cm per sec. was employed. Irradiation of a 6-g sample for 18 hr. produces max. activity due to  $^{55}\text{Mn}$ , whereas the activity of the isotopes of Fe remains negligible, thus permitting activation analysis to be carried out without chemical separation. As the concn. of Mn in the samples increases, the radioactivity ceases to be proportional to the content of Mn, owing to a self-absorption effect. A mean error of  $\pm 2.5\%$  of Mn in ferromanganese is quoted. G. S. ROBERTS

**169. Tris-(*o*-hydroxyphenyl)phosphine oxide as a colorimetric reagent for the determination of ferric iron.** M. J. Holdoway and J. L. Willans (Chem. Div., A.E.R.E., Harwell, Berks., England). *Anal. Chim. Acta*, 1958, **18** (4), 376-380.—The reagent, prepared by demethylating tri-(*o*-methoxyphenyl)-phosphine oxide (Dawson and Burger, *J. Org. Chem.*, 1953, **18**, 207) with  $\text{AlCl}_3$ , is almost specific for Fe. To 5 ml of a soln. of Fe in  $\text{HNO}_3$  (0.3 to 2.5 N) is added 5 ml of a 0.02 M ethanolic soln. of the reagent, the vol. is made up to 50 ml with ethanol and the extinction of the violet-red soln. is read in a Spekker photo-electric absorptiometer, with Ilford yellow-green filter No. 165. Results are referred to a standard curve. The complex is stable for at least 16 hr., and obeys Beer's law over the range 0.02 to 0.1 mg of Fe. The only cation known to interfere is the ceric ion, in amounts about one-half that of the Fe. Of the anions, oxalate interferes strongly in concn. as low as 10 p.p.m., and  $\text{F}^-$  and  $\text{PO}_4^{3-}$  interfere when present in amounts near that of the Fe. R. E. ESSERY

**170. Determination of metal ions with hexamminocobaltic chloride and sodium fluoride.**  
**III. Determination of ferric iron.** Yoshimasa Takashima. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (3), 248-250.—Experiments similar to those for Se (*cf. Anal. Abstr.*, 1959, **6**, 84) were carried out with Fe. The pptn. of  $[\text{Co}(\text{NH}_3)_6]\text{FeF}_6$  is quant. at pH 4-5, the other conditions being the same as for Se. By the use of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  labelled with  $^{60}\text{Co}$ , this method can be extended to 5 to 250  $\mu\text{g}$  of Fe; the specific activity of the reagent should be changed according to the amount of Fe. The error is  $\pm 10\%$  for 5  $\mu\text{g}$  of Fe. K. SAITO

**171. Analytical application of the separation of ferric iron from aluminium employing anionio-exchange resin.** L. D. C. Bok and V. C. O. Schuler (Chem. Dept., Univ. Orange Free State, Bloemfontein, S. Africa). *J. S. Afr. Chem. Inst.*, 1958, **11** (1), 1-8.—Ferric iron is separated from Al by passing a soln. in conc. HCl through a column of Amberlite IRA-400, the  $\text{Fe}^{3+}$  being adsorbed and the  $\text{Al}^{3+}$  passing through; the  $\text{Fe}^{3+}$  are quant. eluted with N HCl. Titanium does not interfere

with the separation, but must be removed from the eluate before the determination of Al. The determination of Fe and Al in cement and in ammonium diuranate is described. I. JONES

**172. Photometric determination of iron in pure tin and tinning baths for steel sheet.** H. Ploum (Max Planck Inst. Eisenforsch., Düsseldorf). *Arch. Eisenhüttenw.*, 1958, **29** (3), 169-172.—The absorption band at 520 to 535 m $\mu$  due to the interaction of  $\text{FeCl}_3$  and thioglycolic acid (I) follows Beer's law for concn. of Fe  $\geq 0.6$  mg per 100 ml, and is unaffected by  $\text{SnCl}_4$  provided that hydrolysis is prevented by excess of acid (HCl, tartaric, or I). The reagent soln. is made by adding 150 ml of I (80%) to 750 ml of aq.  $\text{NH}_3$  (d 0.91) and diluting to 1 litre. The sample (0.25 to 0.5 g) is dissolved in 5 ml of aq. HCl (1:1) with small additions of Br. The soln. is filtered into a 100-ml flask containing  $\approx 4$  ml of HCl (1:1). If the content of Fe in the sample is 0.001 to 0.1%, this soln. (A) is used for the photometric test, by adding to it 20 ml of aq. tartaric acid (25%, w/v) and 20 ml of the reagent soln. If the content of Fe is  $> 0.1\%$ , an aliquot of A is taken containing  $\geq 0.5$  mg of Fe, and in this case the excess of HCl in A must be increased so that  $\approx 4$  ml of 1:1 acid is present in the portion (made up to 100 ml) used for test. The absorption at  $\approx 530$  m $\mu$  is compared with that of a blank soln. and referred to a calibration graph. The test can be carried out in 20 min. Amounts  $\geq 0.08\%$  of Cu, Pb, Bi, As, Sb or Mn do not interfere; Cr and Ni have negligible effects, but Co causes serious error. A. R. PEARSON

**173. Determination of traces of iron in tungsten-cobalt alloy with the aid of paper chromatography.** Yü-Chen Liang (Dept. of Chem., Chung-San Univ.). *Acta Chim. Sinica*, 1958, **24** (3), 205-209.—The determination of contaminating iron in tungsten-cobalt alloys can be carried out with the aid of a descending technique. The alloy is fused with  $\text{Na}_2\text{CO}_3$  in a platinum crucible, then W is removed by pptn. with cinchonine in HCl. In the filtrate, Fe and Co are separated by means of paper chromatography, acetone-water-HCl being used as solvent. The portion of the strip which contains Fe only is cut out and extracted with 0.1 N HCl. Ferric iron is then determined colorimetrically by the  $\text{NH}_4\text{SCN}$  method. For ratios of Fe to Co from 1:50 to 1:3000, the relative errors of the results are reported to be 0.3 to 3%. S. H. YUEN

**174. Cathodic reduction of oxide films on iron.**  
**II. Determination of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ .** K. H. Buob, A. F. Beck and M. Cohen (Nat. Research Council, Ottawa, Canada). *J. Electrochem. Soc., New York*, 1958, **105** (2), 74-78.—The use of the cathodic reduction technique was shown to give accurate measurement of the amounts of  $\text{Fe}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  in a two-scale layer on iron. Examination was made by wt. change, electron diffraction, X-ray diffraction and chemical analysis. There was diffraction evidence of the existence of a thin layer of  $\gamma\text{-Fe}_2\text{O}_3$  between the two layers of oxide. A standard pattern for  $\text{Fe}_3\text{O}_4$  was obtained. C. H. COWPER-COLES

**175. Determination of chief trace elements in pig iron.** T. K. Willmer (Verein für Guszstahlfabr. A.-G., Bochum). *Arch. Eisenhüttenw.*, 1958, **29** (3), 159-164.—Details are given of methods for the determination of Al, Co, Cr, Cu, Mo, Ni, Ti, V, As, Sb, Sn and Pb, selected after co-operative tests in

nine laboratories. Accuracies and times required for each determination are included.

A. R. PEARSON

176. **Electrographical determination of alloying elements in steel.** V. Krajovan-Marjanović, M. Hlavaty, M. Habeković and V. Cuković (Tehnol. Fak. Sveučilišta u Zagreb). *Kem. u Ind., Zagreb*, 1958, 7 (2), 33-38.—An electrographical method for the micro-analytical determination of added elements in alloy steels, by the use of electrolytical tests with filter-paper, and based on Glazunov's studies of the electrochemical properties of metals, has been developed. The apparatus used and the procedures for the determination of Cr, Ni, Co, Mo and V are described.

A. GROCHOWSKI

177. **Photometric determination of beryllium in ferrous metal alloys.** L. P. Adamovich and B. V. Yutsis. *Ukr. Khim. Zhur.*, 1957, 23 (6), 784-787; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,378.—A photometric method is described for the determination of Be with 1-*o*-arsenophenylazo-2-naphthol-3:6-disulphonic acid (thoron) (I). Dissolve 1 g of the material to be analysed in HCl (1:1) and, after removing Si and W, extract the main bulk of the Fe with ether. Add  $H_2SO_4$  and oxidise Cr and V with  $(NH_4)_2S_2O_8$ . Then precipitate Be, Al and the remaining Fe with aq.  $NH_3$ ; Cr, V, Mo, Cu and Ni remain in soln. Dissolve the residue in HCl and treat the soln. with excess of NaOH to remove Fe and Ni. Add I to the filtrate, adjust the pH to  $\approx 12.4$  with a borate buffer soln. and measure the extinction with a green filter in a 20-mm cell, against a comparison soln. containing the same amounts of I and buffer soln. In determining 0.4% of Be, the relative probable error is 2.25%.

C. D. KOPKIN

178. **Excitation of atomic emission lines of nitrogen in steel by means of a high-energy, single-discharge source.** E. F. Runge and F. R. Bryan (Ford Motor Co., Dearborn, Mich., U.S.A.). *Spectrochim. Acta*, 1958, 12 (1), 96-98.—The technique that produced an emission spectrum of N in steel (0.20% of N) is described, and the apparatus, in which the analytical gap is maintained in a  $CO_2$  atmosphere, is illustrated. The spectral range is 3200 to 6500 Å and the line pair N 3994.99 Å - Fe 3961.15 Å was selected for calibration. The coefficient of variation was 17% of the nitrogen present.

E. G. CUMMINS

179. **Photometric determination of arsenic in technical iron with silver diethyldithiocarbamate.** Z. Večera and B. Bieber. *Giessereitechnik*, 1957, 3, 61-64 (in German).—*Cf. Anal. Abstr.*, 1957, 4, 2614.

T. R. ANDREW

180. **Determination of arsenic in iron and steel.** B.I.S.R.A. Methods of Analysis Committee. *J. Iron St. Inst.*, 1958, 188 (4), 331-337.—The colorimetric molybdoarsenate and hypophosphite methods were investigated during the development of a standard method for the determination of As. The latter method was found to be the more reliable.

J. W. O. PYEMONT

181. **Colorimetric determination of microgram quantities of cobalt with *p*-nitrophenylhydrazones of diacetyl monoxime.** Hsi-Hua Hu, Yu-Cheng Leu, Hsueh-Tze Soong and Ping-Tsing Chu (Dept. of Chem., Chungking Medical Coll.). *Acta Chim. Sinica*, 1958, 24 (3), 255-257.—This simple, rapid

determination is based on the formation of a violet-coloured complex of  $Co^{2+}$  with the *p*-nitrophenylhydrazone of diacetyl monoxime (I) (*cf.* Feigl and Goldstein, *Analyst*, 1956, 81, 709) in ammoniacal soln. Ammonium acetate and ethanol are used to destroy the violet colour developed by the interaction between I and aq.  $NH_3$ . Beer's law is obeyed over the range 0 to 5  $\mu g$  of Co per ml of soln. Interference is caused by  $Mg^{2+}$ ,  $Pb^{2+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Zn^{2+}$ .

S. H. YUEN

182. **Determination of cobalt and cadmium in high-purity nickel.** S. E. Kreimer, N. V. Tuzhilina, V. A. Golovina and R. A. Tyabina ("Severonikel" Combine). *Zavod. Lab.*, 1958, 24 (3), 262-264.—Separation of Co from Ni is carried out by pptn. as the complex with diantipyrylmethane and thiocyanate  $(C_{12}H_{14}O_2N_4)_2H_2[Co(SCN)_4]$  and separation of Cd from Ni by pptn. with diantipyrylmethane and iodide or bromide. To determine Co (0.001 to 0.025%), the sample of nickel (1 to 5 g) is dissolved in dil.  $HNO_3$  (3:2) and the soln. is evaporated to fuming with 20 ml of dil.  $H_2SO_4$  (1:1). The salts are dissolved in 100 to 150 ml of water and the cooled soln. is treated with 10 ml of dil.  $H_2SO_4$  (1:1), 15 ml of 20%  $NH_4SCN$  soln. and 25 ml of a 2% soln. of diantipyrylmethane in 0.5 N HCl. After being stirred for 1 hr., the soln. is filtered and the ppt. is washed with a cold 1% soln. of  $NH_4SCN$  until it is free from Ni. The filter and ppt. are heated with  $HNO_3$  and  $H_2SO_4$  to destroy organic matter, and a soln. is obtained for the colorimetric determination of Co with nitroso-R salt. To determine Cd ( $<0.002\%$ ), the sample of nickel (10 g) is dissolved in  $HNO_3$  followed by  $H_2SO_4$ , which is then completely removed by evaporation, and the residue is dissolved in 200 ml of N  $H_2SO_4$ . Addition and dissolution of 2 g of diantipyrylmethane is followed by treatment of the hot soln. with 40 ml of hot 10% KBr soln. The ppt. is collected on the following day and washed with a cold soln. containing 15 ml of conc.  $H_2SO_4$ , 5 g of diantipyrylmethane and 15 g of KBr. Wet oxidation of the ppt. is followed by polarographic determination of the Cd in a basal soln. N in  $NH_4Cl$  and N in aq.  $NH_3$  with the addition of  $Na_2SO_3$  and gelatin. With contents of Cd from 0.0001 to 0.002%, the KBr soln. is replaced by 40 ml of 10% KI soln. After dissolution of the ppt., which contains Cu as well as Cd,  $Na_2S_2O_3$  is added to precipitate Cu, and the Cd is re-pptd. in the filtrate and determined polarographically as described above.

G. S. SMITH

183. **Detection of cobalt and nickel in qualitative analysis.** R. E. D. Clark (Dept. of Science and Technol., Cambes. Tech. Coll. and School of Art, Cambridge, England). *Analyst*, 1958, 83, 431-432.—Nickel sulphide dissolves in an alkaline soln. of quinoxaline-2:3-dithiol to give an intense red soln. Cobalt sulphide also dissolves to give an orange-red soln., but in the presence of excess of  $Na_2S$  only the NiS dissolves. *Procedure*—Precipitate the sulphides of the group-4 cations and wash the ppt. with dil. HCl in the usual way. Transfer minute specks of the black ppt. to 0.5 ml of pyridine containing 0.5 to 5 mg of the zinc complex of toluene-3:4-dithiol and warm the soln. A blue colour indicates Co. Transfer a similar speck to 0.5 ml of a 0.1% soln. of quinoxaline-2:3-dithiol in N NaOH containing 1% of  $Na_2S \cdot 9H_2O$  and heat the liquid to b.p. A red colour, with eventually a red ppt., indicates Ni.

A. O. JONES

**184. Complete chromatographic separation of the tartrate complexes of cobalt and nickel.** V. V. Kulebakina and E. I. Savel'eva. *Nauch. Rabot. Stud. Mosk. Farmatsevt. Inst.*, 1957, (1), 143-148; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,400.—The kinetics of the formation of coloured bands during the separation of the tartrate complexes of Co and Ni on chromatographic alumina by the earlier described method (*Izv. Akad. Nauk SSSR*, 1955, 185-186) is studied. The analytical soln. were prepared by mixing 0.1 M  $\text{CoSO}_4$  and  $\text{NiSO}_4$  with the addition of 0.2 M Na H tartrate in various amounts. The composition-property diagram is obtained, characterising the dependence of the width of the bands due to Co and Ni on the ratio of the concn. of the components. A very sharp separation of the bands has been achieved, which could not be obtained without the use of the complexing reagent. Development of the chromatograms is carried out with water. Cobalt, being the less adsorbable component, may be quant. washed from the column with 0.1 N HCl, while all the nickel remains adsorbed on the column. C. D. KOPKIN

**185. Complexometric determination of nickel without separation in alloys of copper.** I. I. Kalinichenko (S. M. Kirov Ural Polytech. Inst.). *Zavod. Lab.*, 1958, 24 (3), 266-267.—In the presence of borate or acetate the instability of the complexes of Cu with  $\text{S}_2\text{O}_8^{2-}$  is greatly reduced. At pH 8.5 to 9.5, Ni can be titrated with EDTA in the presence of  $\text{Cu}^{2+}$  reduced to  $\text{Cu}^+$  by  $\text{Na}_2\text{S}_2\text{O}_3$ . The sample of copper alloy (0.5 g) containing 4 to 5% of Ni is dissolved in 6 to 8 ml of dil.  $\text{HNO}_3$  (1:1) and the soln. is evaporated nearly to dryness. After addition of water (20 ml), the soln. is treated with 10% NaOH soln. until a ppt. forms. The soln. is cleared by dropwise addition of 50% tartaric or acetic acid soln. and shaken with 20 ml of a soln. containing 540 g of  $\text{Na}_2\text{S}_2\text{O}_3$  in one litre to give a colourless liquid. It is then treated at once with 80 ml of water, 4 drops of 0.2% murexide soln. and 5 ml of a buffer soln. prepared by mixing 20% ammonium acetate soln. neutralised with aq.  $\text{NH}_3$  (5 vol.) with 20% Na acetate soln. (1 vol.) and treating each 100 ml of the mixture with 3 ml of conc. aq.  $\text{NH}_3$ . Titration is carried out with 0.05 N EDTA (disodium salt) to the transition from yellow to reddish violet. G. S. SMITH

**186. Estimation of palladium. I. Picolinic acid as a reagent.** A. K. Majumdar and J. G. Sen Gupta (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1958, 161 (2), 100-103 (in English).—With picolinic acid, Pd is quant. pptd. from slightly acid soln. as a complex of composition  $\text{Pd}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2$ , which is stable up to  $380^\circ$ . All interferences can be masked by EDTA and tartaric acid. The pH range for pptn. is 3 to 7. The ppt. is washed with cold  $\text{H}_2\text{O}$ , dried at  $110^\circ$  and weighed.

**II. Quinaldic acid as a reagent.** A. K. Majumdar and J. G. Sen Gupta. *Ibid.*, 1958, 161 (2), 104-107 (in English).—Palladium is pptd. from a boiling soln. in the pH range 3 to 7 by quinaldic acid as a complex with the composition  $\text{Pd}(\text{C}_{10}\text{H}_8\text{O}_2\text{N})_2$ , which is stable up to  $353^\circ$ . The ppt. is washed with hot water, dried at  $110^\circ$  and weighed. In the presence of  $\text{Hg}^{2+}$ , the Pd is pptd. from a hot soln. at pH 4 and the soln. is kept hot for 15 min. before being filtered. Other interfering ions are masked by tartaric acid and  $\text{NH}_4\text{Cl}$ . G. BURGER

**187. Picolinic acid and quinaldic acid in the separation and volumetric determination of palladium.** A. K. Majumdar and J. G. Sen Gupta

(Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1958, 161 (3), 179-181 (in English).—Palladium can be quant. separated from other ions by pptn. with either picolinic acid (1% w/v soln. neutralised with  $\text{Na}_2\text{CO}_3$ ) or quinaldic acid soln. (2% w/v). A volumetric method of analysis for Pd has been developed in which the ppt. obtained is dissolved in an excess of standardised KCN soln. ( $\approx 0.05\text{ M}$ ), the excess of which is back-titrated with  $\text{AgNO}_3$  soln. Before the titration, 5 ml of aq.  $\text{NH}_3$  (1:1) and 3 ml of aq. 10% w/v KI soln., which acts as an indicator, are added. The end-point is marked by the appearance of a permanent white turbidity. The method is rapid and accurate in the range 2 to 15 mg of Pd with picolinic acid, and 2 to 8 mg of Pd with quinaldic acid. Greater amounts of Pd give low results. S. M. MARSH

**188. Picolinic acid and quinaldic acid in the separation and complexometric determination of palladium.** A. K. Majumdar and J. G. Sen Gupta (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1958, 161 (3), 181-183 (in English).—Palladium can be determined by pptg. it from soln. with picolinic acid (1% w/v soln. neutralised with  $\text{Na}_2\text{CO}_3$ ) or quinaldic acid (2% w/v soln.), and dissolving the ppt. in nickel potassium cyanide. The displaced nickel is then titrated with EDTA (disodium salt). Palladium picolinate dissolves readily on heating in an equiv. amount of nickel potassium cyanide, but it is necessary to boil palladium quinaldate for some time with a slight excess of the reagent. Before titration of the displaced nickel, 5 ml of aq.  $\text{NH}_3$  (1:1) is added to the soln., with 1 to 3 g of  $\text{NH}_4\text{Cl}$  for the quinaldate to prevent pptn. of nickel quinaldate. The indicator used is a solid mixture of murexide and NaCl and the end-point is indicated by a colour change from yellow to purple. The method is accurate and can be applied to the determination of amounts in the range 0.93 mg to 16 mg of Pd. S. M. MARSH

**189. Inorganic chromatography on cellulose. XVII. Separation of the non-volatile platinum metals.** D. B. Rees-Evans, W. Ryan and R. A. Wells (Chem. Res. Lab., Teddington, Middx., England). *Analyst*, 1958, 83, 356-361.—The two solvents used for the separations are hexone (isobutyl methyl ketone) containing 3% v/v of conc. HCl and an oxidising solvent of acidified hexone containing chlorine dioxide (prep. described). The platinum metals are initially present as soln. of their complex chlorides in HCl, and  $\text{ZnCl}_2$  is added to prevent formation of insol. compounds during evaporations with HCl. After removal of  $\text{NO}_3^-$ , if present, by repeated evaporation with HCl, the residue is dissolved in HCl saturated with Cl, treated with repeated additions of the oxidising solvent, the organic layer being decanted on to the cellulose column, and the column is then eluted with the solvent. Platinum and iridium move down the column as a yellow band, the orange-brown palladium band follows, and the rhodium is held at the top of the column until it is eluted with aq. dil. HCl. For the separation of Pt and Ir, the solvent is distilled from the fraction in the presence of water, the aq. residue is repeatedly evaporated with HCl and then dissolved in HCl, and the soln. is treated with  $\text{SnCl}_4$ . Hexone is added and, when the decomposition of the Pt-Sn complex is complete, the hexone layer is applied to the column and the chloroplatinic acid is eluted with the solvent. The reduced Ir is then eluted from the top of the column with acidulated water. A. O. JONES

**190. Chemical concentration and spectrographic determination of some trace elements in silicate rocks.** K. Lounamaa (Central Lab. of the Boliden Mining Co., Skelleftehamn, Sweden). *Suomen Kem., B*, 1957, **30** (5-6), 232-240.—The sample of rock is dissolved with HF. The trace elements (Ag, Bi, Cd, Ca, Cu, Ni, Pb, Sn, Zn), except Sn, are extracted from a basic soln. ( $\text{pH} \approx 9$ ) with dithizone soln. (10 mg in 100 ml of  $\text{CHCl}_3$ ) (I) in the presence of Na tartrate. This extraction is highly satisfactory and the oxidation of I by  $\text{Fe}^{III}$  does not cause trouble. The Fe remaining in the aq. phase is complexed with  $\text{CN}^-$ , the pH adjusted to 5-6, and the Sn is extracted (into  $\text{CHCl}_3$ ) with 1% aq. Na diethyldithiocarbamate soln. (II). A disadvantage in the extraction with II is the necessity of using a weakly acid soln. of  $\text{CN}^-$  with rigorous pH control. The metals from the combined extracts are transferred to a  $\text{MgSO}_4$  matrix and the 10-times enriched sample is spectrographed by using interrupted arc excitation with Cr and In as internal standards. Chromium is very satisfactory and much superior to Pd. The coefficient of variation is 4 to 10%. E. SJÖSTRÖM

**191. Infra-red spectroscopy for determination of mineral constituents of slag and refractories.** W. Pepperhoff (Forschungsinstitut Mannesmann A.-G., Duisburg). *Arch. Eisenhüttenw.*, 1958, **29** (3), 153-158.—The application of the potassium bromide disc technique is described, and transmission spectra at 6 to 14  $\mu$  of systems composed of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ ,  $\text{CaO}$ - $\text{SiO}_2$ ,  $\text{CaO}$ - $\text{P}_2\text{O}_5$ ,  $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ , and  $\text{CaO}$ - $\text{SiO}_2$ - $\text{P}_2\text{O}_5$  are reproduced. The concn. of hydroxy- and fluor-apatite can be determined within  $\pm 1.5\%$  from the relative areas of two bands centred at 16.7 and 17.5 to 18  $\mu$ . A. R. PEARSON

**192. Newer methods available for analysis of glass materials.** M. Paleček (Res. Inst. of Glass, Hradec Králové, Czechoslovakia). *Sklař a Keramika*, 1958, **8** (2), 42-44.—Recent analytical methods and procedures for complexometric determinations of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , Pb, Zn, Ca, Mg, Sr and Ba are reviewed. (64 references.) J. ZÝKA

**193. Improvements in and relating to a method for the determination of the ash content of coal.** Coal Industry (Patents) Ltd. [Inventors: G. J. Pitt and R. R. Gordon]. Brit. Pat. 793,301; date appl. 1.4.54.—A beam of X-rays is directed on to the sample and the degree of absorption of the beam by the material being analysed and the intensity of fluorescent radiation (diffracted selectively by a crystal and measured by a Geiger counter) emitted in response to the X-ray radiation by iron in the material are detected simultaneously and used to obtain the value of the ash content with correction for the iron content. The wavelength of the X-rays used should not exceed that of the iron K absorption edge. J. M. JACOBS

**194. Spectrochemical methods of analysis as applied to mineral matter associated with coal.** K. Dixon (Coal Survey Lab., Gov. Buildings, Chalfont Drive, Nottingham, England). *Analyst*, 1958, **83**, 362-371.—The ground coal-ash (0.1 g) is ignited to remove moisture and  $\text{CO}_2$  and is then fused with  $\text{Na}_2\text{CO}_3$ - $\text{Na}_2\text{B}_4\text{O}_7$ . The internal standard ( $\text{CrO}_3$  in  $\text{HNO}_3$ ) and  $\text{H}_2\text{O}_2$  (to retain Mn and Ti in soln.) are added to the cold melt, which is then extracted with water containing  $\text{HNO}_3$ . Alternatively, the coal (1 g) may be oxidised with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  with a final treatment with  $\text{HClO}_4$ , which

is then removed by evaporation. The residue is extracted with hot water and the internal standard is added. An aliquot (0.05 ml) of the prepared sample soln. is added to a porous electrode (described) which, when dry, is sparked against a high-purity graphite counter-electrode, a second exposure being made similarly, this spectrogram being imposed on the first. Duplicate spectrograms are prepared. Calibration of the spectrograph is carried out with synthetic standards of Specpure materials. Alkali metals are determined by flame photometer, either with the soln. obtained by wet oxidation or with a special soln. prepared by fuming the coal ash with  $\text{H}_2\text{SO}_4$  and HF. The precision of the method is  $\pm 3\%$ . A. O. JONES

See also Abstracts—199. Detection of iodine. **365.** Determination of oxides of nitrogen in air. **366.** Determination of Hg in air. **374.** Determination of I and Br in mineral waters. **379.** Determination of Mo. **380.** Determination of Mn. **382.** Determination of Ba. **383.** Determination of V. **415.** X-ray spectrography of alloys. **418.** Determination of O in steel. **424.** Polarographic technique.

### 3.—ORGANIC ANALYSIS

*Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.*

**195. Rapid determination of carbon and hydrogen in highly volatile combustible organic liquids.** A. R. Panicker and N. G. Banerjee (Central Fuel Res. Sta., Jealgora, Bihar, India). *Analyst*, 1958, **83**, 296-299.—In the apparatus described, the sample of volatile liquid ( $\approx 0.2$  g) is weighed in a specially designed tube that does not require sealing and subsequent breaking in the combustion tube. The volatile portion of the sample is carried in a stream of nitrogen into a stream of oxygen passing through the heated tube, which is charged with oxidised copper gauze, copper oxide, red lead and silver gauze. The absorption train contains anhydrous and soda-asbestos (Carbosorb) for absorption of water and  $\text{CO}_2$ , respectively. Heating of the combustion tube is by means of a three-unit furnace, the second being maintained at  $800^\circ$ , the third at  $350^\circ$  and the first being capable of rapid raising to  $600^\circ$  for the final combustion of any carbonaceous residue left in the sample tube. The advantages claimed for the apparatus are the easy weighing of the sample, the absence of the danger of explosion, the smooth combustion and its suitability for the analysis of low-boiling liquids, e.g., benzene, toluene, petrol and other petroleum distillates. Replicate determinations vary by  $\pm 0.14\%$  for C and  $\pm 0.07\%$  for H.

A. O. JONES

**196. Acidimetric determination of true acetylenic hydrogen in an organic solvent.** M. Micocque and J. A. Gautier (Chaire de Chim. Anal., Fac. de Pharm., Paris). *Bull. Soc. Chim. France*, 1958, (4), 467-469.—The free acid liberated when an acetylenic hydrogen is replaced by Ag is titrated with alkali in pyridine soln. *Procedure*—A pyridine solution of  $\text{AgNO}_3$  (17 g in 100 ml) (5 ml) is neutralised to 1% ethanolic thymolphthalein, and about



0.5 milli-equiv. of the acetylenic compound is added. The soln. is then titrated with 0.1N methanolic NaOH from a micro-burette to a blue end-point. Other acid functions can be titrated similarly before adding  $\text{AgNO}_3$ . Certain acetylenes such as propargyl alcohol, propargyl bromide, and 1-phenylpropynol cannot be determined in this way as the soln. becomes brown.

E. J. H. BIRCH

197. Apparatus for the rapid combustion of volatile organic liquids in the determination of sulphur or halogen impurities. F. Martin and A. Floret (Soc. des Usines Chim. Rhône-Poulenc, Vitry-sur-Seine). *Chim. Anal.*, 1958, **40** (4), 120-126.—The organic liquid is added dropwise to a heated round-bottomed flask and the resulting vapours are carried by means of a current of  $\text{CO}_2$  to a capillary tube which acts as a blowpipe. The vapours are burnt at the end of this tube in a stream of oxygen and the combustion products are aspirated into an absorber of special design which contains a soln. suitable for retention of the impurity to be determined. The method is very rapid, combustion taking place at the rate of about 1 g per minute. The apparatus is described in detail with diagrams. Three procedures are given for the determination of S in benzene. For sulphur contents  $>0.005\%$ , the absorbent used is a standard soln. of barium perchlorate containing thoron reagent. For contents of 0.0015 to 0.006%, a turbidimetric procedure is recommended in which the absorbent is  $\text{BaCl}_2$  soln. For sulphur contents of the order of 0.0001%, the  $\text{H}_2\text{SO}_4$  generated is reduced in a stream of N by a mixture of HI, HCl and  $\text{H}_3\text{PO}_3$ . The  $\text{H}_2\text{S}$  formed is determined colorimetrically after formation of methylene blue by condensation with *p*-aminodimethylaniline and oxidation by a ferric salt. Any  $\text{HNO}_3$  which may be formed, and which interferes with the colorimetric determination, is removed by treatment with  $\text{MgCl}_2$  and a 60:40% Cu-Mg alloy. The method is applicable to benzene and other organic substances such as toluene, acetic acid and white spirit. Halogens may be determined if a suitable absorbent is employed.

S. M. MARSH

198. Analysis of organosilicon compounds for chlorine content. S. V. Syavtsillo, V. T. Shemyatenskova and A. M. Neshumova. *Zavod. Lab.*, 1958, **24** (3), 287-289.—The effectiveness of various media for hydrolysing alkyl- and aryl-chlorosilanes is studied. The best medium is a mixture (1:1) of ethanol and water. After hydrolysis the  $\text{Cl}^-$  are determined by a neutralisation reaction or by mercurimetry. To determine the total content of Cl, the use of Na in liquid  $\text{NH}_3$  (Watt, *Chem. Rev.*, 1950, **46**, 317) is recommended. G. S. SMITH

199. Ultra-micro detection of iodine in inorganic and organic compounds. F. Feigl and E. Jungreis (Lab. da Prod. Min., Min. da Agric., Rio de Janeiro, Brazil). *Z. anal. Chem.*, 1958, **181** (2), 87-92 (in English).—In dilute soln. chloramine T reacts very slowly with tetrabase (4:4'-tetramethyldiaminodiphenylmethane) acetate. A minute trace of iodine catalyses the reaction, yielding immediately a blue oxidation product. The identification limit is 0.0004  $\mu\text{g}$  of iodine. With 1 drop on a spot-plate the dilution limit is 1 in  $1.25 \times 10^3$ ; with 10 ml in a test-tube the dilution limit is 1 in  $2.5 \times 10^3$ . No interference is caused by  $\text{Cl}^-$  or by  $<400 \mu\text{g}$  of KBr. The test can be applied directly to aq. soln.

of iodides. With organic compounds, or if oxidisable contaminants are present, the sample should be ignited with  $\text{MgCO}_3$  in a narrow glass tube and the test made on the residue. G. BURGER

200. Determination of micro amounts of oxygen, carbon monoxide, methane and nitrogen in pure ethylene by adsorption chromatography. H. Pietsch (Dtsch. Erdöl A.-G., Holstein, W. Germany). *Erdöl u. Kohle*, 1958, **11** (3), 157-159.—By using a Linde molecular sieve (5A), the four gases have been determined in the presence of one another. The usual preparative techniques are omitted and the analysis of a 1-litre sample can be completed in 1.5 hr. E. G. CUMMINS

201. Polarographic determination of acetylene, vinyl chloride, 1:2-dichloroethylene, 1:1:2-trichloroethylene and their mixtures. V. Medonos (Inst. Org. Technol., High School Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (1), 31-35.—The method is based on the addition of Br to acetylene (I), vinyl chloride (II), 1:2-dichloroethylene (III) and trichloroethylene in glacial acetic acid. After removing the excess of Br after 24 hr. by bubbling with  $\text{CO}_2$  or H, the soln. is polarographed in 80% acetic acid containing Na acetate. Simultaneous determination of all the compounds is possible with the exception of mixtures of I and III and II and III. J. ŽYKA

202. Continuous gas chromatography. I. Pure acetylene recovery from the end gas of the partial oxidation of methane. M. Freund, P. Benedek, A. László and L. Szepešy (Inst. for Res. of Mineral Oils and Natural Gas, Budapest). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (1-2), 3-18 (in English).—The suitability of gas chromatography for the resolution of this gaseous mixture (6 to 8% of acetylene, 4 to 6% of  $\text{CO}_2$ , 4 to 6% of methane, 25% of CO and 50% of H) has been investigated. Experiments are described which were carried out in either a small assembly, containing 2.5 kg of activated carbon, sufficient for a running of 2 hr., or in a pilot-scale plant. Details of all equipment are included. The material balance on a 65-min. run at the rate of flow of 22 g of carbon per minute shows that pure acetylene was obtained as the lower product at the expense of a small acetylene contamination of the overhead product. Data on capacity, desorption, the distribution of temp., pressure and concn., and the attrition and activity properties of the carbon employed are discussed.

II. Investigation of dynamic adsorption on fixed and moving carbon beds. P. Benedek and L. Szepešy. *Ibid.*, 1958, **14** (1-2), 19-30 (in English).—Fixed-bed experiments to investigate the influence of flow velocity, of acetylene concn., and of the presence of  $\text{CO}_2$  on the dynamic adsorption of acetylene are described. The conclusions drawn, namely that the carbon velocity should equal the advancing velocity of the gas, and that the height of the adsorption zone should be greater than the length of the working zone, have been verified in the laboratory apparatus described in Part I.

III. Investigations of adsorption equilibria of acetylene-carbon dioxide mixtures. P. Benedek and L. Szepešy. *Ibid.*, 1958, **14** (1-2), 31-41 (in English).—Investigations on Nuxit A, the activated carbon used in these experiments, are described. A correlation suitable for the quantitative description of adsorption processes from mixtures has been arrived at, and it has been used in calculations

required for the design of a continuous gas-chromatographic column.

E. G. CUMMINS

203. **Determination of small amounts of carbon tetrachloride by the Fujiwara reaction.** T. E. Burke and H. K. Southern (I.C.I. Ltd., Gen. Chem. Div., Res. Dept., Widnes Lab., Lancs., England). *Analyst*, 1958, **83**, 316.—Numerous modifications of the Fujiwara colorimetric test for chlorinated hydrocarbons involve variations in the concn. and relative amounts of aq. NaOH soln. used, the time and temp. of heating and the interval before comparison of the colour. In most procedures the pyridine and NaOH soln. form two layers, the colour of the pyridine layer being evaluated after separation. The optimum conditions for application to  $\text{CCl}_4$  are described. To 10 ml of anhyd. pyridine containing 0.1 to 1.0 mg of  $\text{CCl}_4$  in a test-tube are added exactly 0.4 ml of 0.1 N NaOH, the lightly stoppered tube is heated in boiling water for 15 min., 5 ml of water is added and the tube is cooled to room temp. The extinction of the liquid, a single layer, is measured absorptometrically with an Ilford No. 604 (green) filter and is referred to a calibration graph. The test as described is of about equal sensitivity for trichloroethylene, tetrachloroethane and  $\text{CCl}_4$ , but is still about three times as sensitive for  $\text{CHCl}_3$ .

A. O. JONES

204. **Determination of water in alcohols with dimethyl oxalate.** J. Koskikallio (Inst. of Chem., Univ. of Helsinki, Finland). *Suomen Kem.*, B, 1957, **30** (5-6), 108-110.—A method developed by Smith (*J. Chem. Soc.*, 1927, 1284), which is based on the stoichiometric hydrolysis of ethyl acetate (I) with respect to the water content in the sample, was modified by substituting dimethyl (or diethyl) oxalate (II) for I. Since II reacts  $10^4$  times as fast as I, the reaction takes place quant. without heat.

**Procedure**—A methanol soln. containing Na methoxide and II, each of 0.2 M concn., is added to the sample in a 50% excess with respect to the water content. The reaction is complete at room temp. within  $>10$  min. if the total vol. of soln. is  $>12.5$  ml. The alkali not consumed is back-titrated with 0.2 M benzoic acid in dry benzene, with cresol red as indicator. The results are accurate to within  $\pm 1\%$ . Advantages compared with the Karl Fischer titration are—(i) the end-point is more distinct; (ii) the reagents are more stable and easily standardised; (iii) the soln. are easy to prepare. Disadvantages are—(i) the method is suitable for water determination in only fairly indifferent solvents, such as alcohols and ethers; in acetone and other ketones, for example, the results are erroneous, owing to condensation; (ii) most acids and bases interfere; (iii) the method is indirect and relatively time-consuming.

E. SJÖSTRÖM

205. **New mass-spectrometric method for determining alcohols and water in complex mixtures. The Fischer-Tropsch product.** S. H. Langer, R. A. Friedel, I. Wender and A. G. Sharkey, jun. (Central Expt. Sta., Bureau of Mines, Bruceton, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1353-1356.—The procedure described can be used to determine glycols, amines and phenols as well as alcohols and water. The alcohols are measured directly after conversion into trimethylsilyl ethers with hexamethyldisilazane. Water does not interfere because it reacts to form

hexamethyldisiloxane, which has a distinctive mass-spectral peak. Paraffins, olefins and other hydrocarbons do not interfere.

K. A. PROCTOR

206. **Estimation of trace and major quantities of lower alcohols, ethers and acetone in aqueous solutions by gas-liquid partition chromatography.** S. J. Bodnar and S. J. Mayeux (Esso Standard Oil Co., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1384-1387.—Ethanediol is used as the stationary phase and ethyl methyl ketone as internal standard in a dual 7-ft. column which allows one sample to be run every 20 min. Water is the last component eluted and does not interfere so long as the sample size does not exceed 0.1 ml. Detection is by thermal conductivity.

K. A. PROCTOR

207. **Rapid spectroscopic method for the determination of water in glycerol.** D. Chapman and J. F. Nacey (Unilever Ltd., Port Sunlight, Ches., England). *Analyst*, 1958, **83**, 377-379.—Use of the near-infrared region, 0.7 to 2.0  $\mu$ , provides a method for the determination of water in glycerol since, in this region, the bonded hydroxyl-group bands of water and alcohols are clearly separated by over 300  $\text{cm}^{-1}$ . A band at 1.93  $\mu$  attributable to absorption due to water is clearly separated from the hydroxyl groups of glycerol at 2.1  $\mu$ . The procedure with a sample of glycerol of unknown water content is to place it in a 1-mm glass cell, scan the 1.9- $\mu$  region, determine the extinction of the 1.9- $\mu$  band, and refer it to a calibration graph. From the limited number of determinations made, the standard deviation is  $\pm 0.06$  over the range 1 to 20% of water in pure glycerol. Results agree satisfactorily with those found by the Karl Fischer method.

A. O. JONES

208. **Polarographic analysis of carbohydrates.** M. S. Shul'man. *Sakhar Prom.*, 1958, (1), 35-37.—The polarographic behaviour of glucose, sucrose, maltose, xylose, arabinose and fructose in the presence of LiCl,  $\text{CaCl}_2$  and  $\text{Ca(OH)}_2$  soln. as supporting electrolytes was studied. It was shown that under specified conditions the polarographic wave height in the presence of  $\text{Ca(OH)}_2$  depends on the chemical structure of the carbohydrate present. Sucrose and raffinose can be determined from the amount of fructose formed by acid hydrolysis with HCl.

SUGAR IND. ABSTR.

209. **Separation and analysis of polyhydroxy substances.** J. X. Khym and L. P. Zill. U.S. Pat. 2,818,851; date appl. 7.2.56.—The degree of formation of acidic borate-complex ions by the reaction of a borate with sugars can be controlled through the borate ion concn. and the pH of the soln. Complexes of high borate content can be adsorbed on a basic ion-exchange resin (borate form) and then desorbed by elution with an aq. soln. of pH 6.5 to 10 containing exchangeable ions which are substantially borate ions. With a mixture of sugars, the process enables the different sugar complexes to be fractionally eluted. The eluates can then be treated with Dowex 50 (H form) and the borate ions can be removed as a volatile alcohol borate; the residual sugars can then be crystallised individually from the residues. This process enables a mixture of sugars to be separated for analysis. The theory of the borate-complex formation and of fractional adsorption and elution processes is discussed in some detail.

SUGAR IND. ABSTR.

**210. Spectrophotometric method for chromatographic analysis of sugars.** C. V. Piper and L. J. Bernardin (Inst. Paper Chem., Appleton, Wis., U.S.A.). *TAPPI*, 1958, **41** (1), 16-18.—A two-stage method of chromophoric development is described. A paper chromatogram of the sugar soln., fully developed with ethyl acetate-acetic acid-water (9:2:2) or butanol-pyridine-water (10:3:3), is sprayed with a soln. of 0.4 g of o-aminodiphenyl in 100 ml of glacial acetic acid and 20 ml of water. The air-dried chromatogram is heated at 105° for 5 min. for partial colour development. Under u.v. light the fluorescent zones are outlined in pencil, then cut out and eluted by shaking for 15 to 20 min. with 6 ml of o-aminodiphenyl reagent, filtered through glass wool and heated in a boiling-water bath till the colour is fully developed, 30 min. for pentoses and 45 min. for hexoses. Blank zones from the chromatogram are similarly treated for use as blanks in the absorptiometric measurement at 380 m $\mu$  of the developed colours. W. HOLDEN

**211. Use of alkaline reagents to determine carbohydrate reducing groups. I. 3:5-Dinitrosalicylate ion and interference by air.** R. T. Bottle and G. A. Gilbert (Dept. of Chem. Biol., City Coll. of Technol., Liverpool, England). *Analyst*, 1958, **83**, 403-406.—Many carbohydrates are unstable in alkaline soln., especially if air is present, and errors are likely to arise in the determination of the reducing groups of a polysaccharide if, simultaneously with the main reaction, oxidative degradation with scission at random points of the carbohydrate chain produces new reducing groups. The influence of O and the concn. of alkali on the reaction of the 3:5-dinitrosalicylate ion with glucose and maltose was investigated. Reactions were carried out in test-tubes, a stream of N being used when exclusion of air was desired. The reaction mixtures with or without de-aeration were heated in a water bath at 65°  $\pm$  0.1° for 30 min. (or in a boiling-water bath for 5 min.), the tubes were quickly cooled and the extinction of the diluted contents at 520 m $\mu$  was measured against a reagent blank. Results showed that removal of O produced a significant increase in the sensitivity and in the linearity of the graph of extinction vs. concn. of sugar. The concn. of alkali should be kept as low as is consistent with rapid reaction rate, and the results suggest an optimum concn. of  $\approx 0.3 M$ . A. O. JONES

**212. Iodimetric determination of formaldehyde in an alkaline medium by conductimetric titration.** D. Ceaușescu (Inst. of Hygiene, Timisoara, Romania). *Stud. Cercet. Chim., Cluj*, 1957, **8** (3-4), 291-295.—In order to obtain a titration curve with a well-defined equivalence point, titration in the presence of NaOH in stoichiometric proportion is recommended. Thus 3 moles of NaOH per mole of iodine are placed in a titration vessel and diluted, and a soln. of formaldehyde is used for titration. During the period of the oxidation-reduction reaction the conductivity drops markedly but, when formaldehyde is in excess, the diminution is less. H. SMER

**213. Qualitative and quantitative determination of aliphatic carbonyl compounds as 2:4-dinitrophenylhydrazones.** K. J. Monty (Johns Hopkins Univ., Baltimore, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1350-1352.—Micromole amounts of mixtures of aliphatic aldehydes and ketones containing up to 14 carbon atoms can be separated, identified and determined as the 2:4-dinitrophenylhydrazones. The derivatives are separated chrom-

atographically on a kieselguhr column with nitromethane as the stationary phase and light petroleum (boiling-range 30° to 60°) saturated with nitromethane as the mobile phase. The fractions are evaporated to dryness and dissolved in benzene, and ethanolic KOH soln. is added to give the required alkaline conditions. The extinction at 425 m $\mu$  and 530 m $\mu$  is plotted against time from the addition of KOH, and the zero-time extinction is obtained by extrapolation. The chromatographic procedure separates the mixture according to the number of carbon atoms in the parent compound. Aldehydes and ketones can be differentiated by the difference in their molar extinction coefficients. These are listed for 17 compounds. G. BURGER

**214. Solvent effects in infra-red spectra of compounds containing the carbonyl group.** L. B. Archibald and A. D. E. Pullin (Queen's Univ., Belfast, N. Ireland). *Spectrochim. Acta*, 1958, **12** (1), 34-40.—The carbonyl stretching absorption of benzophenone, NN-diethylacetamide and NN-diphenylacetamide has been determined in CHCl<sub>3</sub>, 1:2-dichloroethane, methyl cyanide, benzene, CS<sub>2</sub>, CCl<sub>4</sub>, tetrachloroethylene, diethyl ether, cyclohexane and n-hexane. The results are compared with those of Bayliss *et al.* (*cf. Aust. J. Chem.*, 1955, **8**, 26). Band-maxima frequencies, half-intensity band widths, and integrated absorption intensities are tabulated. The possibility of placing solvents in an order of increasing effect on the spectra of the solute mol., irrespective of the solute, is discussed. Band-maxima frequencies increase in the order given for the solvents mentioned above. Approximately linear increases of integrated absorption intensities with decrease of the carbonyl stretching frequency have been found. The shapes and half-intensity band widths are considered briefly. E. G. CUMMINS

**215. Studies on volatile vegetable matters. CXLIX (I). Application of vapour-liquid partition chromatography to mixtures of citrals or certain of their isomeric derivatives.** Y.-R. Naves and A. Odermatt (Lab. de Rech. de L. Givaudan et Cie, S.A., Vernier-Genève, Switzerland). *Bull. Soc. Chim. France*, 1958, (3), 377-384.—Vapour-liquid partition chromatography in a Pyrex-glass tube, 0.45 cm in diam. and 3.6 metres long, is effected on Perkin-Elmer Corp. "C" absorption charge, which has a weak polarity and can be used up to 225°. The carrier gas is H<sub>2</sub> and detection is by thermal-conductivity changes. Analyses of mixtures of isomeric citrals, of nerol and geraniol, of pseudoionones, of ionones, of methylenones, of irones, of citronellols and of linalols, are described and discussed. D. E. J. H. BIRCH

**216. Colorimetric determination of carboxylic acid derivatives as hydroxamic acids.** V. Goldenberg and P. E. Spoerri (Dept. Biochem., Hillside Hosp., Glen Oaks, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1327-1330.—The effect of substituents on the rate of reaction of monocarboxylic acid derivatives with aq. alkaline hydroxylamine has been studied. The time required for maximum hydroxamic acid formation varies from 2 min. to 120 min., according to the structure of the derivative being used.

G. BURGER

**217. X-ray diffraction study of n-alkyl malonic acids.** B. D. Sharma and A. B. Biswas (Nat. Chem. Lab., Poona, India). *Anal. Chem.*, 1958, **30** (8), 1356-1361.—Data are presented for a homologous series from methyl- to octadecyl-malonic acids.

Melting-points and X-ray data are compared with similar series of normal fatty acids and derivatives. Difficulties are encountered in the identification because of polymorphism or stacking disorder in the crystal lattice and because of impurities.

K. A. PROCTOR

**218. The arsenometric determination of oxalate ions.** L. Szekeres, M. Balázsfalvy (née Zergényi) and L. G. Molnár (Dept. of Gen. Chem., Univ. for Agric. Sci., Budapest). *Magyar Kém. Foly.*, 1958, **64** (3), 96-97.—In the presence of Na acetate, oxalate ions are oxidised by Br, prepared from acidified KBr-KBrO<sub>3</sub>. After adding HCl, the excess of Br is back-titrated with As<sub>2</sub>O<sub>3</sub> soln. *Procedure*—To 0.1 N KBrO<sub>3</sub> (10 to 20 ml), containing KBr (15 to 20 g per litre), add 2 N HCl (10 ml) and, after a few minutes, 5 N NaOH (7.5 ml). To the NaOBr thus formed add the unknown Na oxalate soln. ( $\approx 0.1$  N, 5 to 10 ml), and acidify with acetic acid soln. (50%) (5 ml). After 30 min., add conc. HCl (5 ml), and titrate the Br with 0.1 N As<sub>2</sub>O<sub>3</sub> in the presence of 0.1 N alkaline iodine (1 to 2 drops) and starch soln. (1 ml) to a blue endpoint.

A. G. PETO

**219. Rapid analysis of mixtures containing ammonia and methylamines.** N. F. Alekseev, L. G. Yakobson, M. P. Dvinyanina and N. N. Lavrent'eva (Kemerovo Nitrogenous Fertiliser Works). *Zavod. Lab.*, 1958, **24** (3), 283-287.—A scheme, based on a combination of known methods, is described for the determination of NH<sub>3</sub> and mono-, di- and tri-methylamines in admixture.

G. S. SMITH

**220. Tetraphenylboron spot-test for detection of amines and their salts.** F. E. Crane, jun. (Rutgers Univ., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1426-1429.—All basic nitrogen compounds, with the exception of those with ionisation constants of less than 10<sup>-11</sup> and those containing many polar groups, yield a white ppt. or turbidity when a drop of the aq. soln. at pH 3 is treated with a drop of 6% aq. Na tetraphenylboron soln. The detection limits range from 0.13  $\mu$ g to 3  $\mu$ g, with a few exceptions of up to 37  $\mu$ g. The dilution limits range from 1 in 4  $\times 10^6$  to 1 in 1.1  $\times 10^8$ . Interference is caused by K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ag<sup>+</sup>, Tl<sup>+</sup>, Rb<sup>+</sup>, Hg<sup>+</sup>, Hg<sup>2+</sup>, Cs<sup>+</sup> and some organic onium salts. The sensitivity of the test to several compounds is listed.

G. BURGER

**221. Use of sodium tetraphenylboron in quantitative analysis. I. Volumetric determination of aliphatic amines.** E. Yanson, A. Ievin'sh and E. Gudrinietse. *Uch. Zap. Latv. Univ.*, 1957, **14**, 9-16; *Ref. Zhur., Khim.*, 1958, Abstr. No. 43,094.—The method is based on pptn. of the insoluble tetraphenylborates of the amines, and the quant. reaction of the products with HgCl<sub>2</sub>, accompanied by the formation of HCl (4 mol. of HCl for 1 mol. of amine), the quantity of which is determined alkalimetrically. The method may be used for the analysis of secondary and tertiary amines (dibutylamine, triisobutylamine, dipropylamine, diethylamine, triethylamine, etc.). The majority of primary amines give soluble tetraphenylborates, so that it is possible to determine only butylamine satisfactorily. The error of the analysis in the majority of cases is from  $\pm 0.3$  to 0.6%. A table is given of the solubilities of the tetraphenylborates of certain amines.

C. D. KOPKIN

**222. Method for the detection of traces of acrylonitrile [vinyl cyanide].** J. M. Štěpánek and V. M. Černá (Inst. of Hygiene, 48 Šrobárova, Prague). *Analyst*, 1958, **83**, 345-349.—From the system containing vinyl cyanide, a soln. in ethanol or isopropyl alcohol containing 5 to 10 mg of vinyl cyanide per 10 ml is prepared and a 10-ml portion is boiled under reflux with 0.5 g of thiourea and 0.75 ml of conc. HCl. Aq. soln. of vinyl cyanide may be boiled similarly with the reaction mixture. The liquid is subjected to descending paper chromatography with water-saturated *n*-butanol, according to a specified procedure. Chromatograms are prepared from 0.0001 to 0.01 ml of the reaction soln. The dried chromatogram is sprayed with Tollens's ammoniacal AgNO<sub>3</sub> soln. (prep. described) and when the spots of 2-cyanoethylthiuronium chloride have attained their max. colour intensity the chromatogram is washed with water, dried and then washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln. and water. The spot just showing a faint durable grey colour corresponds to 1  $\mu$ g of vinyl cyanide. From the vol. and concn. of the soln. applied to produce this spot the approx. amount of vinyl cyanide per kg of sample is calculated. The preparation of 2-cyanoethylthiuronium chloride for use in the making of comparison chromatograms is described.

A. O. JONES

**223. Determination of simple aliphatic nitriles by reaction with alkaline hydrogen peroxide.** D. H. Whitehurst and J. B. Johnson (Union Carbide Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1332-1333.—Aliphatic nitriles in concn. down to a few p.p.m. can be determined by reaction with a known excess of KOH soln. and H<sub>2</sub>O<sub>2</sub> and titration of the remaining KOH soln. with H<sub>2</sub>SO<sub>4</sub>. The reagents and samples are mixed in a stoppered flask and, after 5 min., with occasional shaking, the flask is fitted with a tube (40 cm  $\times$  10 mm) and the contents are evaporated to a small vol. The standard deviation is 0.5% for pure nitriles and  $\pm 0.15$  p.p.m. for aq. soln. of concn.  $\approx 5$  p.p.m. All compounds that oxidise under these conditions interfere. Corrections can be applied for those compounds that react quantitatively; methanol, ethanol and isopropyl alcohol interfere only slightly. Some amines distil off during evaporation and do not interfere. High results are obtained with pure benzonitrile, acrylonitrile, ethylene cyanohydrin and 3-methoxypropionitrile.

G. BURGER

**224. Two tests for detecting nitriles and amides.** S. Trofimenko and J. W. Sease (Wesleyan Univ., Middletown, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1432-1434.—The tests described are designed to supplement the hydroxamic acid test. (i) The sample is heated with soda lime and the volatile products are distilled into a 1% soln. of CuSO<sub>4</sub> in methanol. Ammonia gives a white turbidity changing to a blue or purple ppt., while amines give ppt. of different colours, enabling amines and other nitrogen compounds to be distinguished from each other and from amides and nitriles. Further confirmation can be obtained by using a wide-range pH indicator in place of the methanolic CuSO<sub>4</sub>. (ii) A methanolic soln. of HgCl<sub>2</sub> and bromothymol blue is added to a saturated soln. of the sample in methanol. The sample is in excess so that on making the soln. alkaline with NaOH a clear blue soln. or a small ppt. shows that the Hg has reacted and thus indicates the presence of an amide with at least one H atom attached to N. Multiple bonds



and  $\alpha$ -H atoms interfere. The limitations of the tests are discussed.

G. BURGER

**225. Gas-liquid partition chromatography of organic sulphur compounds.** C. H. Amberg (Div. of Appl. Chem., Nat. Res. Council, Ottawa, Canada). *Canad. J. Chem.*, 1958, **36** (3), 590-592.—The elution times of thiols, organic sulphides, and alkylthiophenes were measured, the samples being eluted with N from glass columns containing tricresyl phosphate supported on firebrick particles. The eluate was passed into a liquid-nitrogen trap designed to fit on to a mass spectrometer.

P. M. SORGO

**226. Hydrolysis reactions of thioacetamide in aqueous solutions.** E. A. Butler, D. G. Peters and E. H. Swift (Calif. Inst. of Technol., Pasadena, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1379-1383.—The rates of hydrolysis of the thio group and the amide group in thioacetamide have been studied spectroscopically over a range of pH values. It is concluded that thioacetamide can be substituted for  $H_2S$  as a precipitant in acid soln., but in alkaline soln. only under special conditions yet to be studied.

G. BURGER

**227. Analytical application of organic mercury compounds.** M. Wronski (Dept. of Chem. Technol., Univ. of Łódź, Poland). *Analyst*, 1958, **83**, 314-315.—Organomercury compounds of the type R-HgOH form complexes with thiourea, xanthates, thiols and compounds that form ions such as  $S^{2-}$ ,  $S_2^{2-}$ ,  $CS_3^{2-}$  and  $CS_4^{2-}$ . This property can be used for the determination of these types of compound, and, in the presence of suitable indicators, titrations in aq. soln. are possible. Examples of suitable indicators are sodium nitroprusside, diphenylcarbazone, dithione, monomercuriphenolphthalein, thiofluorescein and certain products formed by heating organic compounds with sulphur. With choice of the appropriate indicator one sulphur compound can be titrated in the presence of another. Examples of the methods described are titration of soln. of  $H_2S$  with  $\alpha$ -hydroxymercuribenzoic acid with ethanolic dithione as indicator and the use of thiofluorescein in the titration of mercury in alkaline KI soln. In the last-mentioned method, 10  $\mu$ g of Hg can be determined without interference from other cations such as  $Cu^{2+}$  and Pb.

A. O. JONES

**228. The infra-red spectra of ethoxy- and methyl-ethoxy-polysiloxanes.** Rokuro Okawara (Dept. of Appl. Chem., Fac. of Engng, Osaka Univ., Miyakojima-Ku). *Bull. Chem. Soc. Japan*, 1958, **31** (2), 154-157 (in English).—Characteristic bands due to the  $(Si)OC_2H_5$  group were located near 960 and 1160  $cm^{-1}$ , and near 840  $cm^{-1}$  in ethoxy end-blocked dimethylpolysiloxanes, and near 790  $cm^{-1}$  in ethoxypolysiloxanes.

G. S. ROBERTS

**229. Use of adsorption for isolation of aromatic substances.** A. Asatoor and C. E. Dalgliesh (Postgrad. Med. Sch., Ducane Rd., London). *J. Chem. Soc.*, 1958, 1498-1501.—The study of adsorption on charcoal, partially de-activated by treatment with stearic acid or octadecylamine, is extended to the use of competitive effects in separating adsorbates. Provided that sufficient adsorbent is used, good recovery of minor components of mixtures is possible. The adsorption properties of several compounds are tabulated.

H. F. W. KIRKPATRICK

**230. Infra-red spectra of fulvenes.** J. C. Wood, R. M. Elofson and D. M. Saunders (Res. Council of Alberta, Edmonton, Canada). *Anal. Chem.*, 1958, **30** (8), 1339-1342.—Spectral characteristics for  $CS_2$  and  $CCl_4$  soln. of certain fulvenes are reported. Methylfulvene and dimethylfulvene have been studied and the effects of the addition of benzene rings to the fulvene molecule by fusion or substitution are recorded.

K. A. PROCTOR

**231. Determination of benzene in toluenes.** F. Martin, J. Courteix and S. Vertalier (Soc. de Usines Chim. Rhône-Poulenc, Lab. de Rech. Anal.). *Bull. Soc. Chim. France*, 1958, (4), 494-496.—Toluene (50 to 100 ml) containing benzene is distilled in Martin's apparatus (described) and the temp. of distillation of the first drop (109.9° for 1% benzene and 102.1° for 10% benzene), at a rate of 6 ml per min., gives an almost linear indication of the benzene content in the range. For lower benzene contents the toluene is subjected to gas chromatography with nitrogen as carrier gas and tetraethylene glycol as the liquid phase on firebrick (24 to 28 mesh). At 100° and 1.5 litre of nitrogen per hour, the benzene appears at 12 min. and the toluene at 21 min. Saturated hydrocarbons and acetone are also determined.

E. J. H. BIRCH

**232. Spectrochromatography. I. Determination of isomeric xylenes by gas-liquid chromatography.** J. Franc and J. Jokl (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (2), 276-282.—A new apparatus, which combines absorption spectroscopy and chromatography, has been constructed. Its practical use has been shown by analysing mixtures of aromatic hydrocarbons absorbing in the u.v. region. The method shows great sensitivity, and has been named spectrochromatography. *p*-Xylene (0.005% in *m*-xylene) has been determined. The adsorption material was silica impregnated with 44% dioctyl phthalate or 35% dimethyl 3- and 4-nitrophthalate.

J. ŽYKA

**233. Determination of phenol even in the presence of reducing agents.** E. Schulek and K. Burger (Inst. für anorg. und anal. Chem., L. Eötvös Univ., Budapest). *Z. anal. Chem.*, 1958, **161** (3), 184-191.—The new procedure described, which is applicable to soln. containing 2 to 10 mg of phenol, is based on the reactivity of the fourth bromine atom entering the phenol molecule on direct bromination, which can be determined iodimetrically after the removal of excess of bromine. The soln. to be analysed is made up to 30 to 50 ml with water in a 100-ml Erlenmeyer flask and, if necessary, neutralised to methyl red. Freshly prepared satd. bromine water is added until the mixture becomes red-brown. After 20 min., 20%  $Na_2SO_3$  soln. is added dropwise until the mixture has a yellow tinge. The flask is then shaken and immediately 5 ml of 5% phenol soln. is added in one charge and the mixture thoroughly agitated. At once 0.5 g of KI is added and the mixture is acidified with 5 ml of 20% HCl. After 15 to 20 min. a few drops of starch indicator are added and the liberated iodine is titrated with 0.01 N  $Na_2S_2O_3$ . Results are accurate to within  $\pm 0.5\%$ . For 18 to 60 mg of phenol the procedure is modified slightly. The soln. to be analysed is made up to 100 ml and 50 to 100 ml of satd. bromine water is added in one charge and the mixture shaken energetically. After 30 min. the procedure is completed as described above, except that 10 ml of 20% HCl is used for acidification, and titration of

the liberated iodine is carried out with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . The results are accurate to within  $\pm 1\%$ . The method is reliable even if greater amounts of reducing agents such as sulphite and sulphide are present. Since phenol is converted immediately into tribromophenol bromide under the conditions used, the reaction mixture is free from side products such as tribromophenol and tetrabromophenol.

S. M. MARSH

**234. New method for the quantitative determination of the principal constituents of technical phenol mixtures.** L. Rappen (Ges. für Teerverwertung m.b.H., Duisburg-Meiderich). *Brennst. Chem.*, 1958, **39** (5-6), 65-74.—The content of phenol, the cresols, the xyleneols, 2:3:5-trimethylphenol, and 5-ethyl-3-methylphenol in technical phenol mixtures from coal tar is estimated by the determination of m.p. of mixtures of the commercial phenol with the pure individual phenols, and reference to tables showing contents *vs.* m.p. The pure phenol is added in such a quantity as to bring the mixture m.p. within a specified range. J. L. PROSSER

**235. Analysis of polyhydric phenol mixtures.** W. Beckering and W. W. Fowkes (Lignite Exp. Sta., Region III, U.S. Bureau of Mines, Grand Forks, N.D., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1336-1338.—Addition of Pb acetate and Na acetate soln. to mixed tar acids precipitates the lead salts of catechol and 4-alkylcatechols, which can be removed by filtering and washed free from other tar acids with acetone. The mol. wt. of a 4-alkylcatechol can be determined by drying and weighing the lead salt, decomposing it with  $\text{HNO}_3$  and determining the Pb as sulphate. 3:6-Disubstituted catechols are not pptd. and 3-monosubstituted catechols are pptd. only from aq. soln. in the absence of other tar acids or organic solvents. G. BURGER

**236. Preliminary study of a colorimetric method for anisole determination.** M. R. F. Ashworth (Inst. for Org. Chem., Univ. of the Saar, Saarbrücken). *Anal. Chim. Acta*, 1958, **18** (4), 330-333.—Results are given for the effect of time of heating, amounts of formaldehyde and anisole, and moisture on the colour reaction between anisole, formaldehyde and  $\text{H}_2\text{SO}_4$  in glacial acetic acid at  $50^\circ$ . The intensity of colour increases rapidly for the first 30 min., but is almost constant from 45 to 120 min. The optimum ratio for formaldehyde and anisole under the given conditions was 2:1. Moisture has a marked influence, and reagents must be protected from it. To the anisole soln. in glacial acetic acid add 1 ml of formaldehyde soln. (2 ml of 35% diluted to 100 ml with glacial acetic acid). Make up to 5 ml with glacial acetic acid, heat at  $50^\circ$  for 1 hr., and measure the extinction of the warm soln. in a 14-mm cuvette at 490  $\mu$ . The calibration curve is not rectilinear. Benzene gives no colour, but influences the colour development with anisole; the calibration curve is more curved with 0.2 ml of benzene than without it, but could be used to determine up to 2% of anisole in benzene. R. E. ESSERY

**237. Infra-red spectra of the benzenecarboxylic acids.** F. González-Sánchez (Inst. Nac. Combustible, Zaragoza, Spain). *Spectrochim. Acta*, 1958, **12** (1), 17-33.—The infra-red spectra of 12 benzenecarboxylic acids and their four hydrates have been measured from 2 to 15  $\mu$  as mulls in liquid paraffin. An analysis of their structure is

attempted and discussed. No free O-H stretching bands were detected. Five bands throughout the range have been attributed to the -COOH group. The one at 900  $\text{cm}^{-1}$  disappears in the hydrates. Deviation from the existing correlations for determination of the type of benzene-ring substitution are attributed to the electrophilic -COOH group. E. G. CUMMINS

**238. Fluorimetric determination of o- and m-hydroxybenzoic acids in mixtures.** G. A. Thommes and E. Leininger (Kedzie Chem. Lab., Michigan State Univ., E. Lansing, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1361-1363.—The acids can be determined in the concn. range 0 to 12 p.p.m. with a relative error of  $<5\%$  by excitation at 314  $\mu$  under various pH conditions. At pH 5.5 only the o-isomer fluoresces, whilst at pH 12 both isomers fluoresce. The p-isomer does not fluoresce under the conditions employed and therefore does not interfere. K. A. PROCTOR

**239. Acidimetric analysis of nitrocyclohexane.** V. S. Khallov, B. B. Brandt and G. N. Shcherbova. *Khim. Nauka i Prom.*, 1957, **2** (6), 806; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,496.—The method is based on the isomerisation of primary and secondary nitro compounds into salts of acid isonitro compounds in the presence of alkali. To 1 to 5 ml of a 1 to 2% soln. of nitrocyclohexane (I) in ethanol add a one- or two-fold excess of 0.1 N KOH. After 2 or 3 min. titrate the excess of alkali in the presence of phenol- or thymol-phthalein. Acids which are titrated at pH  $>9$  are determined together with I. Their content is determined by a direct titration of the sample with alkali, with the same indicator. The accuracy of the method is  $\pm 1\%$ . C. D. KOPKIN

**240. Modified method for the determination of polycyclic hydrocarbons.** B. T. Commins (Medical Res. Council, Dunn Lab., St. Bartholomew's Hospital, London). *Analyst*, 1958, **83**, 386-389.—The method described is a modification of that of Cooper (*Analyst*, 1954, **79**, 573) and involves the separation of the hydrocarbons on alumina columns with cyclohexane as solvent and eluent, and subsequent spectrophotometric determination of the hydrocarbons in successive fractions of the eluate. As in the method of Cooper (*loc. cit.*), the peak height is measured from a base line joining two points on the wavelength-extinction graph on either side of the peak but, to reduce error due to overlapping spectra, the separation between the two selected wavelengths is reduced to 8  $\mu$ . The method is applied to the determination of polycyclic hydrocarbons in smoke samples collected in and around diesel-bus garages. The accuracy with which polycyclic hydrocarbons can be determined depends largely on their complete separation. Repeated determinations of the same sample extract showed a coeff. of variation of  $\approx 10\%$  and indicate that results of single samples are within  $\pm 25\%$  of the mean value. A. O. JONES

**241. Determination of naphthalene in [coal] gas.** The solubility of picric acid in water and the dissociation of naphthalene picrate. A. B. Densham and L. A. Raval (Fulham Res. Lab., North Thames Gas Board, London). *J. Appl. Chem.*, 1958, **8** (4), 267-270.—This method is based on the absorption of naphthalene by aq. picric acid soln. The naphthalene picrate which separates is removed by

filtration and titrated as picric acid with standard NaOH soln. The concn. of the picric acid soln. is critical since, unless an almost saturated soln. is used, some naphthalene passes through unabsorbed; if the concn. of picric acid is too high, a fall in ambient temp. will cause pptn. of free picric acid. These factors have necessitated the careful determination of picric acid solubility in the range 0° to 30°, corrected values for which are given. Erroneous results may also arise from the dissociation of naphthalene picrate. The loss of naphthalene may be reduced by maintaining one absorber at 0°; alternatively, it is possible to apply a correction. A detailed discussion of the derivation of this correction is given. G. S. ROBERTS

**242. Gas-chromatographic analysis of mixtures of tetralin and decalin.** A. Castiglioni (Inst. für Warenkunde, Univ. Turin, Italy). *Z. anal. Chem.*, 1958, **161** (3), 191-192.—A mixture of tetralin and commercial decalin (containing both *cis*- and *trans*-isomers) can be separated into its components and quant. analysed by gas-liquid chromatography. A stainless-steel column (6 mm internal diam. and 2 metres long) is packed with Celite C22 impregnated with 25% dodecyl phthalate. The column is maintained at 176° and hydrogen (8 litres per hr.) is used as the carrier gas. The retention times are 2 min. 40 sec. for *trans*-decalin, 4 min. 20 sec. for *cis*-decalin and 10 min. 40 sec. for tetralin. After calibration of the column, quant. analyses can be carried out with the use of the resulting chromatograms. Results are accurate and the analysis can be carried out in 15 min. on very small amounts of material (0.04 ml). S. M. MARSH

**243. Chromatography and detection of certain N-substituted phenothiazines.** R. L. Tabau and J. P. Vigne (Lab. des Isotopes du Centre de Lutte contre le Cancer, Marseille, France). *Bull. Soc. Chim. France*, 1958, (4), 458.—*Procedure*—Various N-substituted phenothiazines are chromatographed on Whatman No. 1 paper by the descending technique with acetone - M Na acetate - M acetic acid (2:4:1, by vol.) as solvent, without previous equilibration of the paper. Distilled water and acetone containers are placed in the bottom of the tank. The rate of flow is  $\approx 25$  cm at 20° in 6 hr. The spots are detected by iodine or bromine vapours, iodo-bismuthate reagent, fluorescence in u.v. light or photography at 2537 Å. Phenothiazine itself remains at the origin. E. J. H. BIRCH

**244. Determination of traces of water in hydrocarbons in gasoline boiling range. Sample handling and interferences.** J. W. Loveland, T. B. Webster, C. P. Hablitzel and G. W. Reed (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1316-1321.—The technique and apparatus described enable samples to be collected and titrated with Karl Fischer reagent without the sample, solvent or reagent coming into contact with atmospheric moisture. The sample bottles, with their neoprene cap closures, are dried for 8 hr. at 150° F before use. The titration vessel is a 500-ml 5-necked flask fitted with a magnetic stirrer, platinum electrodes for electrometric end-point indication, a neoprene cap for admission of the sample, a guarded vent, an exit tube for emptying by suction and a burette with a reagent reservoir. All air vents are guarded with desiccant tubes. The sample is transferred to the titration vessel by a syringe passed through the neoprene cap. The solvent is titrated in the flask before addition of the

sample. A correction for interference by thiols can be made by drying a sample and titrating.

G. BURGER

**245. Colorimetric determination of phosphorus in gasolines containing tritoly phosphate.** F. F. Hoffman, L. C. Jones, jun., O. E. Robbins, jun., and F. R. Alsberg (Shell Oil Co., Wood River, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1334-1336.—The method described is suitable for the control of blending. The sample (1 to 2 ml), containing 20 to 50  $\mu$ g of P, is evaporated almost to dryness at 90° to 100° under an air stream and the residue is decomposed by heating with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. Water (25 ml) is added and the soln. is neutralised with NaOH soln. The heteropoly blue colour is developed by adding 5.5 N H<sub>2</sub>SO<sub>4</sub> (5 ml), 2.5% ammonium molybdate soln. (2 ml) and 0.5% hydrazine sulphate soln. (2 ml) and heating for 10 min. on a boiling-water bath. The soln. is cooled and diluted to 50 ml and the extinction is measured at 825 m $\mu$ . Results are referred to a calibration curve. One analyst can perform 15 determinations per day. The coeff. of variation is  $\approx 1.4\%$ . Other constituents normally present in petrol do not interfere. G. BURGER

**246. Quantitative determination of tetraethyl-lead in fuel.** K.-H. Braun (VEB Sachsenring, Kraftfahrzeug- u. Motorenwerk, Zwickau, Germany). *Chem. Tech., Berlin*, 1958, **10** (3), 159.—Tetraethyl-lead is treated with Cl<sub>2</sub> to form the chloride, which is extracted with water, and the Pb is complexed and back-titrated with ZnCl<sub>2</sub> soln. The petrol (100 ml), KClO<sub>4</sub> (4 g) and conc. HCl (20 ml) are allowed to react, then 20 ml of water is added and the mixture is shaken thoroughly. The lower water layer is drawn off and the petrol layer is washed with 20 ml of water. The combined water extracts are heated until a solid separates, then diluted with 300 ml of water and neutralised with aq. NH<sub>3</sub>. Buffer soln. (54 g of NH<sub>4</sub>Cl and 350 ml of conc. aq. NH<sub>3</sub> in 1 litre) (10 ml), 0.01 M EDTA (25 ml) and Eriochrome black T indicator (0.3 g) are added, and the soln. is titrated with 0.01 M ZnCl<sub>2</sub> to a red-violet colour. J. L. PROSSER

**247. Identification and determination of low-boiling phenols in low-temperature coal tar.** C. Karr, jun., P. M. Brown, P. A. Estep and G. L. Humphrey (Bureau of Mines, Morgantown, W. Va., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1413-1416.—A mixture of 12 components containing phenols, cresols, xylenols and ethylphenols was analysed by gas-liquid chromatography on a column (12 ft.  $\times$  0.25 in.) packed with firebrick (30 to 60 mesh), containing 31% by wt. of di-n-octyl phthalate. The column temp. was 160°, He was used as the carrier gas, flowing at 150 ml per min. (inlet press. 15 p.s.i.g., outlet press. 1 atm.) and the sample size was 250  $\mu$ l. Components were identified by their relative retention times and determined by the area under the peaks. The results were in agreement with those obtained by fractional distillation followed by i.r. spectrometry. Some phenols were not resolved under these conditions.

G. BURGER

**248. Qualitative and quantitative analysis of heavy tar oils by gas chromatography.** F. Dupire and G. Botquin (Lab. de Recherches, S.A. Carbochim., Tervre, Belgium). *Anal. Chim. Acta*, 1958, **18** (4), 282-290 (in French).—An easily constructed apparatus, described and illustrated, comprises a

column of Pyrex glass (250 cm × 6 to 8 mm), filled with refractory brick (60 to 80 mesh) containing 30% of silicone grease as stationary phase. The column is sealed after filling to avoid the use of ground glass or silicone rubber connections, and inserted in a furnace consisting of a Pyrex-glass tube wound with resistance wire and asbestos. Detection is by means of a pair of platinum-wire catharometers and an electronic recorder is incorporated to trace the chromatographic curve. With 5 to 10  $\mu$ l of sample, and 50 ml per min. of He at 350 mm pressure, an analysis can be completed in 30 to 60 min. at 200° to 250°, according to the type of oil being analysed. Solid samples are dissolved in benzene (1:1) and 20  $\mu$ l of the soln. is examined. Quant. analysis is carried out by the method of "internal normalisation," which consists in equating the sum of the areas under the peaks of the curve to 100, when the proportions of the areas under the individual peaks give the percentages directly. This renders the results independent of the actual operating conditions. Retention times relative to naphthalene are given for several aromatic hydrocarbons for various column temperatures. Analyses of known mixtures gave good replication. Figures are quoted for the analysis of samples of naphthalenic, wash, and anthracene oils.

R. E. ESSERY

**249. Photometric determination of carbon deposit in lubricating oil after use in diesel motors.** B. Bernelin (Inst. Franç. Pétrole, 2, Rue de Lubeck, Paris). *Rev. Inst. Franç. Pétrole*, 1958, **13** (3), 259-266.—The dispersed C in sump oil is determined rapidly from the extinction at 500 m $\mu$  of a dilution of 5 g of oil in 1 litre of benzene. A little detergent may be added to the diluent to prevent flocculation. Beer's law is obeyed and the results correlate closely with gravimetric tests provided that allowance is made, with vehicle sump oils, for inorganic material of low opacity.

A. R. PEARSON

**250. Chromatographic analysis of brown-coal tar according to chemical compound type.** E. Leibnitz, W. Schmidt and E. Gundermann (Inst. für org. Grundstoffchem., Leipzig). *Brennstoffchem.*, 1958, **39** (5-6), 87-90.—A method for the chromatographic fractionation of brown-coal tar according to predominant chemical type is described. The first chromatogram is run on acid alumina with the heptane-soluble asphalt-free fraction in soln. in light petroleum (boiling-range, 30° to 60°). The blue zone containing azulene is removed, and the remainder of the column is extracted with several solvents in sequence, to give a series of solns., which are themselves chromatographed in order to obtain the compound types. The subsequent columns are made from SiO<sub>2</sub> activated at 350°; phenols and bases are separated on alumina. J. L. PROSSER

**251. Reproducible procedure for the determination of mineral impurities in organic substances by calcination. Application to the analysis of glues and gelatins.** A. Clavier and J. Pouradier (Lab. de Recherches de la Société Kodak-Pathé). *Chim. Anal.*, 1958, **40** (4), 114-117.—Results are presented which indicate the behaviour of glues and gelatins and of certain of their mineral impurities [CaCO<sub>3</sub>, SiO<sub>2</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgSO<sub>4</sub>] at temp. up to 1000°, and also the behaviour of the ash during cooling. It is concluded that the three main sources of error are—(i) losses that may occur during swelling at 200° to 500°, (ii) chemical changes (e.g., decomposition of carbonates, chlorides,

nitrites) that occur at 500° to 1000°, (iii) the regain in weight of the ash that occurs during cooling due to the uptake of CO<sub>2</sub> and water vapour. The following standard method is suggested. Calcination is carried out in an electric furnace, the temp. of which is raised to 850° over a period of 5 hr. and maintained at this temp. for < 1 hr. The sample is placed in a dish (10 cm in diam. and 5 cm in depth, for 10 g) in order to eliminate losses due to swelling. The ash is cooled in a desiccator containing 200 g of CaO and left overnight before weighing. The reproducibility of results obtained under these conditions is 1 to 2%.

S. M. MARSH

**252. Analysis of non-ionic surfactants.** S. Siggia (General Aniline and Film Corp., Central Res. Lab., Easton, Pa.). *Soap, N.Y.*, 1958, **34** (3), 51-53, 133.—A review of techniques for identifying and determining non-ionic surfactants is presented. Aspects surveyed include (i) characterisation, i.e., identity of the non-ionic surfactant as a whole, identity of the hydrophobic portion and the ratio of hydrophobic to hydrophilic parts; (ii) cloud points; and (iii) separation by extraction and ion exchange. The quantitative methods indicated cover a wide range of concn. G. HELMS

**253. Determination of the content of essential oils in the flowers of *Rosa damascena* Mill., with special reference to plant selection.** D. Ivanov, C. Ivanov, N. Marékov and I. Ognianov (Univ. of Sofia, Bulgaria). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (1-2), 163-171 (in French).—The apparatus devised for this micro-determination on 100 to 250-g samples is illustrated and the method (distillation and measurement of the oil) is described. Reference is made to the different composition of the extract obtained by the method of Bobiler (cf. *Maslobolno-Zhirovaya Prom.*, 1953, **3**, 21) in which activated carbon adsorption is used for recovering the oil from the distillate.

E. G. CUMMINS

**254. Determination of hydrocarbons in cosmetic products.** M. Zahradník and V. Pokorná (Pražské Kosmetické Závody, Prague). *Průmysl Potravin*, 1958, **9** (3), 143-145.—If a soln. of the sample in light petroleum is passed through a column of Al<sub>2</sub>O<sub>3</sub> or silica gel, esters, higher fatty alcohols and acids are retained, whilst hydrocarbons remain in the soln. and can be determined by drying (70°) and weighing after evaporation of the solvent.

J. ZÝKA

**255. Identification of unknown synthetic fibres.** S. G. Smith (Security Mills, Inc., Newton, Mass., U.S.A.). *Amer. Dyest. Rep.*, 1958, **47** (5), 141-142, 145.—A method for the qual. analysis of Dacron, nylon, viscose, acetate, Arnel, Darlan, Acrilan, Creslan, Orlon, Zefran, poly(vinyl chloride), alginate, Dynel, Verel, Vicara and Saran synthetic fibres is described and discussed. Primarily microscopical, the system involves observation of fibre morphology and optical behaviour between crossed polarisers, as well as the direction of movement of the Becke line and degree of fibre visibility. The observations are made with the sample immersed successively in one or more of 4 mounting liquids of known refractive index. Solubilities are determined when necessary or desired for further confirmation. Accuracy, speed, small sample size and freedom from dye stripping are among the advantages of the method. E. S. LANE



256. Method for removing cotton or viscose in the analysis of fabrics containing nylon blends. W. S. Sondhelm and H. Webster. *J. Text. Inst. Trans.*, 1958, **49** (3), T171-T172.—The arrangement of the nylon fibres is maintained if the area over which the cellulosic component is to be removed by immersion in cuprammonium hydroxide is not much greater than the length of the nylon staple used in the blended yarn, and if the cellulosic component outside the area of removal is protected, by the method described, with polyethylene.

O. M. WHITTON

257. Analysis of amino-formaldehyde resins. J. C. Morath and J. T. Woods (American Cyanamid Co., Bound Brook, N.J.). *Anal. Chem.*, 1958, **30** (8), 1437-1440.—Methods for the determination of amines, formaldehyde and methanol in amino-formaldehyde resins are summarised.

G. BURGER

258. Determination of hydroxyl value. C. P. A. Kappelmeier and J. Mostert (Kunstharzfabriek Synthese N.V., Katwijk aan Zee, Holland). *Verf. kroniek*, 1958, **31** (2), 61.—Difficulties in some existing methods for the determination of hydroxyl value, when applied to alkyl resins, are indicated. The most promising procedure is acetylation of the sample dissolved in toluene, with acetyl chloride in the presence of pyridine, followed by addition of  $H_2O$  and ethanol, and titration with alcoholic KOH.

L. A. O'NEILL

259. Detection of phthalic acid isomers and benzoic acid in alkyl resins by infra-red absorption spectrometry. M. L. Adams and M. H. Swann (Coating and Chem. Lab., Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1322-1324.—The acids, in the form of dried films, have specific absorption characteristics in the  $11\text{-}\mu$  to  $15\text{-}\mu$  region.

K. A. PROCTOR

260. Analytical spectroscopy in the protective coatings industry. C. A. Lucchesi (Sherwin Williams Co., Chicago, U.S.A.). *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1958, **30**, 212-230.—The use of u.v. and i.r. absorption spectroscopy for the examination of paint media, flame photometry for the determination of drier metals, and X-ray fluorescence spectrometry for the analysis of pigments is described. A novel feature is the use of i.r. absorption spectra for the examination of extender pigments, and some typical spectra are shown.

L. A. O'NEILL

261. Analysis of paints, lacquers and varnishes. N. W. Hanson (I.C.I., Ltd., Wexham Rd., Slough, England). *J. Oil Col. Chem. Ass.*, 1958, **41** (3), 203-257.—Methods are given in detail for separation of pigment from the medium, and for identification and determination of the constituents of the pigment mixture and of the solvent, oil, plasticiser and resinous and polymeric constituents of the medium and of minor constituents (wetting agents and colloids) in emulsion paints. Examples are given of the procedures used for different types of product.

S.C.I. ABSTR.

262. Methods of testing vulcanised rubber. Parts B1 to B5. Preparation of material and extraction methods. British Standards Institution (2 Park St., London). B.S. 903: Parts B1 to B5, 1958, 13 pp.—In this revision of the 1950 edition the method of determining paraffin wax and ceresin is omitted and an alternative apparatus for the acetone extraction is included. The parts cover the preparation

of the material for analysis, and methods of determination of the acetone extract, the unsaponifiable matter in acetone extract, the chloroform extract, and the alcoholic potash extract.

O. M. WHITTON

263. Infra-red quantitative analysis data. *Anal. Chem.*, 1958, **30** (8), 1441.—The following data have been published under the co-operative programme between *Analytical Chemistry* and the Coblenz Society of the U.S.A. Analysis of acrylic acid, ethylbenzene, methyl methacrylate,  $\alpha$ -methylstyrene, styrene and vinyl cyanide mixtures, R. T. Scheddel.

See also Abstracts—87, Determination of B in boranes. 86, Determination of Sc in coal ash. 153, Determination of U in coal ash. 277, Determination of ethanol and acetaldehyde in plants. 287, Determination of cellulose. 338, Determination of piperazine salts. 355, Determination of water in glycerol. 367, Determination of benzanthrone in air. 375, Determination of trichloroethylene in waters. 376, Determination of petroleum products in sewage. 422, Gas-detecting apparatus.

#### 4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

264. The composition of normal and pathological urine with an estimate of the concentration of unanalysed substances. H. J. Yardley (Dept. of Exp. Path., Univ. of Birmingham, England). *Clin. Chim. Acta*, 1958, **3** (3), 280-287.—The cationic content of urine is mainly  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $NH_4^+$ , and  $Cl^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$  and  $HCO_3^-$  represent about 80% of the anions normally present. Subtraction of the v.p. of the urine from the calc. v.p. due to urea, creatinine and inorganic ions shows about 20% of unanalysed constituents. Total solids content gives similar results. Deviations from normal in some pathological urines examined are reported.

H. F. W. KIRKPATRICK

265. Spectrochemical analysis of certain macro and minor elements in plant ash using a constant-current generator. A. Strasheim and R. J. Keddy (Nat. Phys. Res. Lab., C.S.I.R., Pretoria). *J. S. Afr. Chem. Inst.*, 1958, **11** (1), 21-32.—In the method described, a constant d.c. arc is used as light source. The dependence of the results on the electrode parameters is shown. The analytical results of a group of test samples are given and discussed for the elements K, Mg, Na, Ca, Ba, Sr, Mn, Fe, Al and Cu.

I. JONES

266. The assay of mixtures of sodium-24 and potassium-42 in clinical tracer studies; with particular reference to the measurement of exchangeable sodium and potassium. D. S. Munro, H. Renschler and G. M. Wilson (Dept. Pharmacol. Therap., Univ. Sheffield). *Phys. in Med. Biol.*, 1958, **2**, 239-254.—Several physical and chemical methods of determining  $^{24}Na$  and  $^{42}K$  in a mixture are described. The physical methods involved the use of Veal-type Geiger-Müller counters of wall thickness 30 mg per sq. cm and 200 to 300 mg per sq. cm, or of scintillation counters with different thicknesses of crystal

housing. In a third physical method an end-window was used with an aluminium filter of thickness 260 mg per sq. cm which could be placed between sample and counter tube. The first method was the most rapid and had certain other advantages over the others, but the physical methods generally are inaccurate when the proportions of the two nuclides are very unequal. In the first chemical method, K is pptd. first as potassium cobaltinitrite and then as KH tartrate; in the second, pptn. is by means of sodium tetraphenylboron. The second method was found to be quicker than the first and equally accurate. Both chemical methods are more accurate within an equal period of time than the physical ones, especially when  $^{40}\text{K}$  forms only a small proportion of the mixture. A rapid method of measuring exchangeable body K and Na is described in which  $^{40}\text{K}$  and  $^{24}\text{Na}$  are used. The dose to the patient during the procedure is calculated as  $>0.15$  rad (1 rad equals 100 ergs per g of absorbed radiation), much lower than that in previous procedures.

NUTR. ABSTR. REV.

267. New micro-method for the colorimetric determination of calcium in serum and urine. M. E. Chilcote and R. D. Wasson (Dept. of Biol. Chem., Univ. of Buffalo Sch. of Med., N.Y., U.S.A.). *Clin. Chem.*, 1958, 4 (3), 200-210.—Prepare a murexide-NaCl powder by grinding together 0.1 g of dye and 54 g of NaCl and store in a desiccator. For use, mix 0.5 g with 3.0 ml of 0.25 N KOH until dissolved, add 22 ml of cold  $\text{H}_2\text{O}$  and place in an ice bath. For each serum determination, pipette 5.0 ml into a cuvette cooled in ice, allow to warm until condensation ceases, place in the spectrophotometer and adjust to zero absorption at 490 m $\mu$ . Add 50  $\mu$ l of serum, mix the soln. by bubbling air through, and read the absorption. Treat standard soln. similarly in the range 2 to 16 mg of Ca per 100 ml.

H. F. W. KIRKPATRICK

268. Simple procedure for the single sample determination of serum copper and iron. B. Zak (Dept. of Path., Wayne State Univ. Coll. of Med., Detroit Mich., U.S.A.). *Clin. Chim. Acta*, 1958, 3 (4), 328-334.—Copper is determined by addition of 2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline (bathocuproin) sulphionate and measurement of the absorption at 485 m $\mu$ . The absorption at 535 m $\mu$  is also read as a correction in the iron determination. 4:7-Diphenyl-1:10-phenanthroline (bathophenanthroline) sulphionate is then added to the same soln. and the absorption is read at 535 m $\mu$ . Subtraction of the reading due to the copper complex at this wavelength gives the corrected iron-complex value.

H. F. W. KIRKPATRICK

269. Spectrophotometric determination of copper and zinc in animal tissues. J. T. McCall, G. K. Davis and T. W. Stearns (Florida Agric. Expt. Sta., Gainesville, U.S.A.). *Anal. Chem.*, 1958, 30 (8), 1345-1347.—This rapid and accurate method is based on the difference between the extinctions of a soln. containing both copper- and zinc-zincon complexes and of the same soln. after destroying the zinc complex with EDTA (disodium salt). These metal complexes are stable for 1 hr. and their extinctions at 610 m $\mu$  follow Beer's law over the concn. range 0.1 to 2.4 p.p.m. Interfering ions (those of Co, Mn, Ni, Al, Mo, Be, Bi, Cd and Fe) are removed by pptn. as the hydroxides.

K. A. PROCTOR

270. Determination of mercury in human urine. U.K.A.E.A., Industrial Group (Chem. Services Dept., Capenhurst, England). U.K.A.E.A. Report IGO-AM/CA-174, 1958, 6 pp.—Oxidise an aliquot (50 ml) by heating in a water bath at 80° to 90° for 20 min. with 18 M  $\text{H}_2\text{SO}_4$  (5 ml) and  $\text{KMnO}_4$  (1 g). Add 35% hydroxylamine hydrochloride soln. (2 ml), cool, transfer to a separatory funnel and dilute with  $\text{H}_2\text{O}$  to approx. 100 ml. Extract with 0.01% dithizone in  $\text{CCl}_4$  ( $2 \times 5$  ml followed by 2-ml aliquots) until the  $\text{CCl}_4$  remains green. Shake the combined dithizone extracts with 0.1 M HCl (5 ml) to remove interfering metals; wash the acid extract with dithizone (2 ml) before discarding. Extract the Hg by shaking the combined dithizone soln. with 5 M HCl ( $2 \times 5$  ml), wash the acid extracts with  $\text{CCl}_4$  (3 ml) and dilute with water to 100 ml. Titrate with 0.0005% dithizone in  $\text{CCl}_4$  in 1-ml portions by shaking and separating until the  $\text{CCl}_4$  layer remains green.

H. F. W. KIRKPATRICK

271. Note on the serum-iron determination described by Peters, Giovannelli, Apt and Ross. T. Peters and T. J. Giovannelli (Mary Imogene Bassett Hosp., Cooperstown, N.Y., U.S.A.). *J. Lab. Clin. Med.*, 1958, 51 (3), 494.—It is recommended that 0.02% of bathophenanthroline (4:7-diphenyl-1:10-phenanthroline) dissolved overnight in isopropyl alcohol be substituted for the same reagent in isopropyl alcohol-isomyl alcohol (3:1) in the earlier method (cf. Peters et al., *Anal. Abstr.*, 1957, 4, 3053).

W. H. C. SHAW

272. An instrument and method for the automatic, rapid, accurate and sensitive titration of chloride in biological samples. E. Cotlove, H. V. Trantham and R. L. Bowman (Nat. Heart Inst., U.S. Dept. Health, Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1958, 51 (3), 461-468.—The method is based on the coulometric generation of  $\text{Ag}^+$  and amperometric indication of the end-point. A constant d.c. is passed between two silver generator electrodes so that the amount of  $\text{Ag}^+$  liberated into the sample is proportional to time. The timer incorporated in the instrument is automatically stopped when the current between a pair of silver indicator electrodes increases by a pre-set amount when pptn. of all  $\text{Cl}^-$  is complete. The method will determine 0.25 micro-equiv. of  $\text{Cl}^-$  and titrations may be completed in 5 sec. or more according to the precision required. Details for constructing the instrument are given.

W. H. C. SHAW

273. Micro-method for the determination of butyl alcohol-extractable hormonal iodine in serum. N. E. Kontaxis and D. E. Pickering (Pediatric Endocrine and Metab. Res. Unit, Univ. of Oregon Med. Sch., Portland, U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1958, 18 (7), 774-786.—The *n*-butanol extraction of Taurog and Chaikoff (*J. Biol. Chem.*, 1948, 176, 639) and the alkaline ashing procedure of Barker et al. (*J. Clin. Invest.*, 1951, 30, 55) are applied to 0.5 ml or less of serum. The final colorimetric procedure includes spectrophotometric measurements made possible by stopping the reaction with  $\text{AgNO}_3$ .

H. F. W. KIRKPATRICK

274. Simple determination of blood alcohol for the clinical laboratory. A. Mather (Memorial Hosp., Wilmington, Del., U.S.A.). *Clin. Chem.*, 1958, 4 (3), 223-231.—The sample is steam-distilled and the ethanol in the distillate is determined colorimetrically with dichromate reagent.

H. F. W. KIRKPATRICK

275. Determination of blood alcohol. Improvements in chemical and enzymatic procedures. P. L. Kirk, A. Gibor and K. P. Parker (Sch. of Criminology, Univ. of Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1418-1422.—An improved dichromate oxidation method is described. It includes distillation in a special apparatus with precautions for eliminating interfering substances. A simplified diffusion method, in which liver alcohol dehydrogenase and co-enzyme I are used, is also described.

H. F. W. KIRKPATRICK

276. Optimum conditions of the acid dichromate method for determining ethanol in body fluids. L. Wilkinson (Dominion Lab., Christchurch, New Zealand). *Analyst*, 1958, **83**, 390-396.—A review of the many modifications of the original Nicloux method suggests that a detailed knowledge of the mechanism of the dichromate-ethanol reaction might lead to simplification of the quant. method. A study of the rates of reaction at room temp. of  $K_2Cr_2O_7$  and ethanol in concn. of  $H_2SO_4$  ranging from 5 N to 37 N indicated that optimum acid conditions lie between 18.5 N and 23 N, and that rates of reaction increase with increasing concn. of  $K_2Cr_2O_7$ . Rates of reaction of probable interfering substances also depend on acid concn. The comparatively low reaction rates of these interfering substances at room temp. with 0.05 N  $K_2Cr_2O_7$  in 10 N  $H_2SO_4$  suggest that a diffusion technique would be suitable. The necessary conditions can be attained in Conway micro-diffusion cells. With  $K_2CO_3$  in the centre cell, diffusion is complete in 2 hr. and interference by other likely constituents of the body fluids is negligible.

A. O. JONES

277. Determination of ethanol and acetaldehyde in plant tissue by low-temperature diffusion. H. G. Wager (Low Temp. Sta. for Res. in Biochem. and Biophys., Cambridge Univ., England). *Analyst*, 1958, **83**, 291-295.—Ethanol and acetaldehyde are transferred from the frozen tissue into aq.  $H_2SO_4$  by evaporation and diffusion. The apparatus is a crystallising dish covered with a glass plate, having a small hole in it sealed with a glass slide. Inside is a glass tripod supporting a wire tray to hold the sample (peas). A calculated amount of  $H_2SO_4$  (66% v/v) is placed in the dish by weighing and the whole apparatus is cooled to  $-12^\circ$ . The peas at  $-20^\circ$  are added to the dish, the weighted lid is put on and the apparatus is maintained at  $-12^\circ$ . For peas the transfer of ethanol and acetaldehyde is complete in 70 to 100 days. The sample is removed at room temp. and the acid is reduced to 50% v/v by addition of water through the hole in the lid and weighing. An aliquot of the acid is withdrawn and added to sufficient pure  $H_2SO_4$  to make the concn. exactly (6 + 1). Acetaldehyde is determined in this soln. by a modification of the method of Barker and Summerson (*J. Biol. Chem.*, 1941, **138**, 534), and ethanol in an aliquot of the acid in the dish by iodimetric titration of reduced  $H_2CrO_4$ . The results obtained by the diffusion method are lower than those of a distillation method. The diffusion method is considered preferable as enzymic changes and other decompositions are retarded at low temp.

A. O. JONES

278. Determination of volatile phenols in urine. S. L. Tompsett (N. Gen. Hosp., Edinburgh, Scotland). *Clin. Chem.*, 1958, **4** (3), 237-240.—The differential determination of *p*-cresol and phenol in urine is described.

H. F. W. KIRKPATRICK

279. Method for the determination of urinary meprobamate. E. S. Harris and J. J. Reik (Wyeth Inst. for Med. Res., Radnor, Pa., U.S.A.). *Clin. Chem.*, 1958, **4** (3), 241-245.—Meprobamate is hydrolysed in NaOH soln. and the  $NH_3$  determined by nesslerisation. *Procedure*—To 10 ml of urine in a 60-ml separating funnel add 5.0 ml of 0.2 M phosphate buffer (pH 7.4) and extract with ether (2 × 30 ml). Reduce the vol. of combined ether extracts to 5 to 10 ml and transfer to a column (6 mm × 100 mm) of filter-paper powder prepared by slurring with ether. Wash the column with dry ether. Evaporate the ether eluate to dryness and determine the  $NH_3$  after distillation with NaOH, colorimetrically with Nessler reagent. Compare the result with a standard soln. of meprobamate in urine treated similarly.

H. F. W. KIRKPATRICK

280. Determination of  $\beta$ -substituted glutarimides in blood: time-concentration curves after intravenous injection of two barbiturate antagonists. K. W. Anderson (Nicholas Inst. for Med. and Vet. Res., Sherbrooke, Victoria, Australia). *J. Pharm. Pharmacol.*, 1958, **10** (4), 242-248.—A rapid spectrophotometric method is given for the determination of bemegride ( $\beta$ -ethyl- $\beta$ -methylglutarimide) (I) and  $\beta$ -tetramethyleneglutarimide (II) in blood. Recoveries are >90% with a standard deviation between duplicates of  $\pm 1.5\%$ . The method is used to show the rapid removal of I and II from blood after intravenous injection. *Procedure*—Shake the heparinised blood (2 to 5 ml containing <100  $\mu$ g of I or II) with  $CHCl_3$  (30 ml) for 30 min. Chill a 10-ml aliquot of the  $CHCl_3$  layer to  $0^\circ$  and extract with 0.04 N NaOH (5 × 10 ml) at  $0^\circ$ . Centrifuge the combined alkaline extracts under refrigeration to remove suspended  $CHCl_3$  and measure the extinction at 230  $m\mu$  against a blank similarly prepared from glutarimide-free blood.

A. R. ROGERS

281. The photometric micro-determination of blood glucose with glucose oxidase. A. Saifer and S. Gerstenfeld (Jewish Chronic Disease Hosp., Brooklyn, N.Y., U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (3), 448-460.—The method is based on the use of a commercial enzyme preparation (Glucostat reagent) containing glucose oxidase, which is specific for  $\beta$ -D-glucose, and peroxidase. In the presence of glucose oxidase, glucose is oxidised to gluconic acid and  $H_2O_2$ , which then reacts with *o*-dianisidine in the presence of peroxidase to give a colour proportional to the glucose in the heparinised blood-sample. A colorimetric and spectrophotometric modification are described. The various factors affecting the final colour are studied, and results are compared with those given by conventional blood-glucose methods.

W. H. C. SHAW

282. Detection of glycosuria in pregnancy: comparative study of glucose oxidase and copper reduction techniques. M. M. Chertack (Univ. Illinois Coll. Med., Chicago). *J. Amer. Med. Ass.*, 1958, **166**, 48-49.—Over 1000 samples of urine from pregnant women were examined for glucose by Benedict's reagent and Clinistix and by the glucose oxidase reagents, Clinistix and Tes-tape. The latter were most sensitive and were specific for glucose.

NUTR. ABSTR. REV.

283. Electrophoresis of free sugars in blood. H. M. C. Robinson and J. C. Rathbon (War Memorial Children's Hosp., London, Ont., Canada). *Science*,

1958, 127, 1501-1502.—Differentiation of glucose, galactose, fructose and lactose in deproteinised blood is made by paper electrophoresis with borate soln. at two different pH values. The method is satisfactory for concn. from 4 mg to about 125 mg per 100 ml of any of these sugars. *Procedure*—Blood (0.1 ml) is pipetted into ice-cold 95% ethanol (2 ml), chilled in ice for 15 min. and centrifuged at 2000 r.p.m. for 5 min. The supernatant fluid is removed and evaporated to dryness, the residue is dissolved in 0.05 ml of  $H_2O$  and the soln. is applied to the paper strips. Electrophoresis is carried out for 4 hr. at 210 V, the strips are dried, dipped in aniline hydrogen phthalate soln. [redist. aniline (930 mg) and phthalic acid (1.66 g) dissolved in acetone (95 ml) and water (5 ml)], and dried at 125° for 10 min. Compact, stable brown spots denote the sugars. The borate buffer soln. are—(i) 2% aq.  $Na_2B_4O_7 \cdot 10H_2O$  soln., pH 9.2; (ii) 24.8 g of  $H_3BO_3$  and 5.8 g of NaCl dissolved in about 700 ml of  $H_2O$ , 0.05 M  $Na_2B_4O_7 \cdot 10H_2O$  is added until the pH is 7.0 and the soln. is diluted to 1 litre with  $H_2O$ . H. F. W. KIRKPATRICK

284. Estimation of free sugars in skeletal muscle of codling (*Gadus callarias*) and herring (*Clupea harengus*). N. R. Jones (Torry Res. Station, Aberdeen). *Biochem. J.*, 1958, 68 (4), 704-708.—Ribose, but not glucose, in extracts of herring and codling muscle reacts readily with nitrogenous constituents during chromatography, and electrolytic desalting interferes with the determination of ribose. Removal of salts and amino N by suitable mixed ion-exchange resins, followed by lyophilisation, paper chromatography, elution of the sugars from the paper, and determination absorptiometrically, gives values for the glucose and ribose contents accurate to within  $\pm 6\%$ . J. N. ASHLEY

285. The reaction of pentoses with anthrone [determination of pentose sugars]. R. W. Bailey (Plant Chem. Lab., D.S.I.R., Palmerston North, New Zealand). *Biochem. J.*, 1958, 68 (4), 669-672.—The formation of a thermostable blue-green colour by reaction of D-xylose, D- and L-arabinose, and D-ribose with anthrone in the presence of 70% (v/v)  $H_2SO_4$  depends mainly on the concn. of the anthrone, excess of which rapidly destroys the colour. Conditions for the determination of pentoses by the anthrone reaction are defined. J. N. ASHLEY

286. Enzymic determination of myo-inositol. A. Weissbach (Nat. Inst. Health, Bethesda, Md., U.S.A.). *Biochim. Biophys. Acta*, 1958, 27 (3), 608-611.—The method is based on the use of an extract of *Aerobacter aerogenes* cells grown on a myo-inositol medium to catalyse the reduction of diphosphopyridine nucleotide (I) by myo-inositol. The preparation of the extract is described. In the presence of the extract the reduction of I depends on the amount of myo-inositol (up to 0.12  $\mu$ mole per test), which is determined from the increase in extinction at 340 m $\mu$ . The reaction is inhibited by colchicine, but the other cyclitols and sugars tested did not interfere. W. H. C. SHAW

287. Micro-determination of cellulose in studies with cellulase. G. Halliwell (Rowett Res. Inst., Bucksburn, Aberdeenshire). *Biochem. J.*, 1958, 68 (4), 605-610.—The cellulose is washed with water or other solvents on a sintered-glass filter-stick. It is then oxidised stoichiometrically with  $H_2SO_4$ -

$K_2Cr_2O_7$ , and the excess of  $K_2Cr_2O_7$  is determined titrimetrically or, more conveniently, colorimetrically. The amount of cellulose is calculated as anhydroglucose from a glucose calibration graph. The method is applicable to the determination of 0.2 mg (average recovery 97%) to 1.1 mg (average recovery 100%) of cellulose, and it can be used for cellulose powder, swollen cellulose, hydrocellulose and dewaxed cotton fibres. The procedure is used to determine cellulolysis by the cellulase of *Myrothecium verrucaria*. J. N. ASHLEY

288. Estimation of alginic acid in seaweeds by the method of colloid titration. Satoshi Okimasa (Hiroshima Women's Coll., Japan). *Bull. Agric. Chem. Soc. Japan*, 1958, 22 (2), 63-68.—Positive and negative polymer ions combine stoichiometrically in dilute soln. at a definite pH value, and the determination described is based on this reaction. *Procedure*—Immerse 1 to 2 g of finely cut dried seaweed in 0.1 N Cl soln. (50 ml) for 1 hr., decant the liquid and repeat until the material is fully bleached, drain, and wash with water. Extract the alginic acid with  $Na_2CO_3$  soln. (1%, w/v, 125 ml) at 80°, filter and dilute the filtrate to 250 ml with water. Test for the presence of protein. When protein is present, neutralise a 5-ml aliquot with 0.1 N HCl, add HCl-KCl buffer soln. (pH 1.8) (5 ml) and 0.3% pepsin soln. (2 ml). Digest at 40° for 20 hr.; neutralise with aq.  $NH_3$  and add water (20 ml). To the deproteinised soln. add 0.005 N N-trimethylated glycol chitosan (cf. Senju and Okimasa, *J. Agric. Chem. Soc. Japan*, 1950, 23, 432) and 2 drops of 0.1% toluidine blue indicator. Adjust the pH of the soln. to  $\approx 7$ . Shake well, set aside for a few minutes and titrate with a 0.0025 N soln. of poly(potassium ethylenesulphonate). The end-point is indicated by a colour change from blue to reddish purple, also by the sudden pptn. of the reactants. H. B. HEATH

289. Quantitative paper partition chromatography of sialic acids. E. Svennerholm and L. Svennerholm (Dept. of Med. Biochem., Univ., Gothenburg). *Nature*, 1958, 181, 1154-1155.—To separate N-acetylsialic acid (I) and N-glycolylsialic acid (II), develop 100- $\mu$ g amounts on Whatman No. 1 paper, which has been washed in turn with 0.1 N HCl,  $H_2O$  and  $CHCl_3$ -methanol (2:1), with n-butanol-n-propanol-0.1 N HCl (1:2:1) as mobile phase. After development for 18 hr., allow the paper to dry, spray with resorcinol reagent or Ehrlich's reagent and heat at 100° for 10 or 15 min. To prepare the resorcinol reagent, dissolve resorcinol (1 g) and trichloroacetic acid (15 g) in 50% aq. ethanol (20 ml) containing 0.1 M  $CuSO_4$  (0.2 ml) and dilute to 60 ml with n-butanol. The  $R_F$  values are: I, 0.45, II, 0.34. Alternatively, elute the sialic acid zones from the chromatogram with  $H_2O$  and analyse by the resorcinol reaction; the accuracy is  $\pm 3\%$ . A. R. ROGERS

290. Determination of polyunsaturated acids in lipids of plasma and tissue. R. T. Holman and H. Hayes (Hormel Inst., Univ. of Minnesota, Austin, U.S.A.). *Anal. Chem.*, 1958, 30 (8), 1422-1425.—The method consists in extraction of the lipids, isomerisation by treatment with alkali, and measurement of the u.v. absorption at 375, 346, 315, 268 and 233 m $\mu$ . Equations derived from values given by pure polyunsaturated acids after isomerisation are used for calculating the proportions of these constituents. H. F. W. KIRKPATRICK



291. **Circular paper chromatography of long-chain fatty acids in the analysis of bacterial lipopolysaccharides.** A. Nowotny, O. Luderitz and O. Westphal (Dr. A. Wander-Forschungsinstit., Freiburg-Zähringen, Baden). *Biochem. Z.*, 1958, **330** (1), 47-52.—A modification of the circular paper chromatography technique of Kaufmann and Nitsch (*Anal. Abstr.*, 1955, **2**, 2557) for the separation of fatty acids is described. Copper acetate-ferrocyanide staining is used for the detection of saturated fatty acids, but exposure to  $\text{OsO}_4$  vapour permits selective staining of unsaturated fatty acids. Application of this technique to the identification of the components of a mixture of long-chain ( $\text{C}_{10}$  to  $\text{C}_{24}$ ) fatty acids in acid hydrolysates of 11 species of Gram-negative bacteria is reported.

G. W. CAMBRIDGE

292. **Determination of the flavonols in the presence of their 3-glycosides. I. The determination of quercetin in the presence of rutin.** D. G. Constantinescu and R. Oteleanu. *Stud. Cercet. Chim., Acad. R.P.R.*, 1957, **5** (3), 395-407.—In an investigation of the difference of intensity of coloration given by quercetin and rutin with  $\text{UO}_2^{2+}$ , the theory that the complexes formed are of different structure is confirmed by work on the complexes formed with  $\text{SbCl}_5$ . The absorption curves of the  $\text{SbCl}_5$  complexes in the visible spectrum differ because in certain concn. the extinction values ( $E_{547}^{1\%1\text{cm}}$ ) for the rutin- $\text{SbCl}_5$  complex are zero, whereas those for the quercetin complex are appreciable even in much weaker soln. A photometric method for the determination of 0.05 to 100 parts of quercetin in the presence of 100 parts of rutin has been devised on the basis of this difference.

H. SHER

293. **Spectrophotometric measurement of bilirubin concentrations in the serum of the newborn by the use of a micro-capillary method.** D. White, G. A. Haidar and J. G. Reinhold (William Pepper Lab. of Clin. Med., Univ. of Pennsylvania, Philadelphia, U.S.A.). *Clin. Chem.*, 1958, **4** (3), 211-222.—Capillaries of uniform internal diameter (1.20 to 1.21 mm external) and a max. variation of 0.01 mm are used. Four capillaries are used for each serum measurement. Blood is collected to a length of 5 to 6 cm and the opposite end is sealed in a small flame. After clotting has occurred, the capillaries are centrifuged at 10,000 r.p.m. for 1 min. and the portion containing the serum is cut off and the length of serum column is measured accurately. Each capillary is rinsed into 1.0 ml of phosphate buffer (7.65 g of  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  and 1.74 g of  $\text{KH}_2\text{PO}_4$  dissolved in water to 1 litre, pH 7.4) in a cuvette, and the extinction is read at 455 and 575  $\text{m}\mu$ . Subtraction of the extinction at 575  $\text{m}\mu$  from that at 455  $\text{m}\mu$  provides a simple correction for haemolysis.

H. F. W. KIRKPATRICK

294. **New improved test for urobilinogen in urine. (A method of eliminating indican.)** Toichiro Sawada, Yozo Shibata and Yoshitawa Kuroda (Fac. of Med., Kyushu Univ., Fukuoka, Japan). *Kyushu J. Med. Sci.*, 1958, **9** (1), 15-21.—The reaction mixture of urine and Ehrlich's reagent is extracted three times with toluene to remove colour due to indican. The aq. soln. is then chromatographed on paper with methanol-water (3:2) as solvent.

H. F. W. KIRKPATRICK

295. **Routine assay of [vitamin] B<sub>12</sub> in serum.** A. I. Tiffin and G. M. Williamson (Dept. of Bact., Sch. of Med., Leeds, England). *J. Clin. Path.*,

1958, **11** (3), 224-226.—Details are given of a microbiological method suitable for occasional use; reproducible results are obtained in assays carried out at very long intervals.

H. F. W. KIRKPATRICK

296. **Fluorimetric measurement of plasma adrenaline and noradrenaline concentrations in man, monkey and dog.** G. F. Mangan and J. W. Mason (Walter Reed Army Med. Center, Washington, D.C., U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (3), 484-493.—From a study of the method of Weil-Malherbe and Bone (*Biochem. J.*, 1952, **51**, 311), it is concluded that the method is suitable for determinations of adrenaline and noradrenaline in physiological experiments. Recovery at plasma concn. of 0.02 to 0.1  $\mu\text{g}$  was  $103.8 \pm 9.4\%$  and  $79.1 \pm 13.8\%$  for the respective compounds.

W. H. C. SHAW

297. **Extended use of the Kingsley biuret reagent.** A. C. Kibrick (Div. of Chem., N.Y. Veterans Admin. Hosp., N.Y., U.S.A.). *Clin. Chem.*, 1958, **4** (3), 232-236.—Protein in cerebrospinal fluid is determined by mixing the sample with an equal vol. of reagent (*J. Lab. Clin. Med.*, 1942, **27**, 840). The method is also applicable to protein in urine by pptg. with trichloroacetic acid and redissolving in 2% NaOH soln.

H. F. W. KIRKPATRICK

298. **Determination of amino acids by double isotope-dilution technique.** J. K. Whitehead (Radiochem. Lab., Barnato-Joel Lab., Middlesex Hosp. Med. Sch., London). *Biochem. J.*, 1958, **68** (4), 662-668.—Acetic anhydride labelled with  $^{14}\text{C}$  and  $^3\text{H}$  is used in a double isotope method for the determination of amino acids in hydrolysates from 2  $\mu\text{g}$  of a protein. The acetylated amino acids are separated by paper chromatography. The individual spots are cut out, the paper is burnt, the  $^{14}\text{CO}_2$  and  $^3\text{H}_2\text{O}$  are collected, and the radioactivity of each is determined. There is good general agreement between the results and those obtained by microbiological assay or column chromatography.

J. N. ASHLEY

299. **Polarographic determination of amino acids containing thiol and disulphide groups.** D. B. Coult (Chem. Section, Chem. Defence Exp. Estab., Porton Down, Salisbury, Wilts., England). *Analyst*, 1958, **83**, 422-425.—Linear calibration graphs are prepared with soln. of the particular amino acid to be studied in the K1000 cathode-ray polarograph. Soln. of unknown concn. are adjusted to 0.05 N HCl and the peak height obtained is referred to the calibration graph. Sera are denatured and deproteinised by heating in a boiling-water bath with *o*-mercaptobenzoic acid. The filtered liquid (2 ml) is then added to 3 ml of 0.05 N HCl and the concn. of amino acid is determined polarographically. Serum (1 ml) is hydrolysed by boiling with 20 ml of 5 N HCl under reflux for 8 hr. and the soln. is then diluted to 200 ml. Penicillin is treated with 0.1 N NaOH and then warmed with excess of 0.1 N HCl to convert it into penicillamine. The soln. is diluted to a known vol. with 0.05 N HCl. The method has been used to follow the reaction between cysteine and nitrogen mustard gas HN2.

A. O. JONES

300. **Identification of amino acids in fresh and fermenting grape juices.** K. Hennig and P. Ventner (Inst. f. Biochemie & Weinchemie der Lehr- und Forschungsanstalt f. Wein-, Obst- und Gartenbau, Geisenheim, Germany). *Naturwissenschaften*, 1958,

45 (6), 130.—Fermented juice is filtered to remove spores. The interference of minerals, proteins and carbohydrates is overcome by employing electrophoresis in the first run and chromatography in the second dimension on filter-paper. The buffer for electrophoresis is formic acid - acetic acid - water at pH 1.9, and 1600 to 1800 V at 20 to 30 mA is used. Chromatography is carried out at right angles to the electrophoresis with phenol-water (7:3, w/v). Up to 20 amino acids may be detected. Some amino acids, e.g., glycine, serine,  $\gamma$ -aminobutyric acid, threonine, cystine and asparagine, are unexpectedly absent in some juices. E. KAWERAU

301. Clearing free amino acid solutions of plant extracts for paper chromatography. P. H. Plaisted (B.T. Inst. for Plant Res. Inc.). *Contr. Boyce Thompson Inst.*, 1958, 19, 231-244.—The ethanolic plant extract is passed through a column of Dowex 50-X8(H) (200 to 400 mesh) packed in 80% ethanol which retains the amino acids. The acidic and neutral amino acids and amides are eluted with 0.4 N aq.  $\text{NH}_3$  in ethanol followed by washing with ethanol-water. The basic amino acids are completely removed by percolation with 4 N aq.  $\text{NH}_3$  in water. Later the  $\text{NH}_4^+$  are removed from the eluting soln. by drying under vacuum. E. G. BRICKELL

302. Quantitative method [for the determination of] lysine by high-voltage paper electrophoresis. Einosuke Tamura and Fumi Yokota. *Ann. Rep. Nat. Inst. Nutr., Tokyo*, 1957, 35.—Lysine, arginine and histidine, and also aspartic and glutamic acids, were separated by paper electrophoresis (2400 V) in phthalate buffer (pH 5.9). After separation, lysine was dissolved in 50% ethanol, and determined spectrophotometrically at 570 m $\mu$  as the ninhydrin compound. Figures for the lysine contents of beef, pork and chicken muscle were somewhat higher than those obtained by microbiological assay on the same samples. M. D. ANDERSON

303. New absorption peak of tyrosine. Z. P. Zein-Eldin and B. Z. May (U.S. Fish and Wildlife Service, Galveston, Tex., U.S.A.). *Science*, 1958, 127, 1055-1056.—Autoclaving at relatively high pressures (70 to 90 lb per sq. in.) of dil. tyrosine soln. (1 to 100 mg per litre) in the presence of alkali concn. ranging from 0.12 to 5.0 N gives rise to a peak at 330 m $\mu$ . Tyramine, 3;5-di-iodotyrosine and *p*-hydroxybenzoic acid behave similarly; other amino acids showed no spectral change. Plasma and crystalline albumin showed the same peak after autoclaving. H. F. W. KIRKPATRICK

304. Quantitative interpretation of results after agar electrophoresis. I. J. Uriel (Pasteur Inst., Paris, France). *Clin. Chim. Acta*, 1958, 3 (3), 234-247.—The method of Graber and Williams (*Bull. Soc. Chim. Biol.*, 1955, 17, 67) has been used for investigating the measurement of the protein bands after staining with Amido black, and a suitable procedure is described.

II. Proteins and lipoproteins of normal human serum. J. Uriel. *Ibid.*, 1958, 3 (4), 384-396.—Methods of calculating electrophoretic mobility and quant. distribution are described. H. F. W. KIRKPATRICK

305. Simple and accurate method for the determination of fibrinogen in blood. E. Gachev and D. Mutavchiev (Res. Inst. for Childhood and Motherhood Care, Sofia, Bulgaria). *Lab. Delo*, 1958, 4

(2), 3-7.—Fibrinogen is determined absorptiometrically by means of the biuret reaction. E. HAYES

306. Turbidimetric analysis of fibrinogen and  $\gamma$ -globulin with ammonium sulphate by different photometric techniques. N. S. Rafferty, A. G. Tyrol, jun., and I. A. Parfentjev (Dept. of Microbiol., Yale Univ. Sch. of Med., New Haven, Conn., U.S.A.). *Clin. Chem.*, 1958, 4 (3), 185-193.—Measurement of Tyndall light in a nephelometer enables turbidimetric determinations of protein concn. to be made over the range 0.025 to 0.3%. Colorimetry is less sensitive, but may be used to extend the range of measurement to 3% of protein. H. F. W. KIRKPATRICK

307. Determination of total protein in lipaemic sera by means of the biuret reaction. E. Gachev (Res. Inst. for Childhood and Motherhood Care, Sofia, Bulgaria). *Lab. Delo*, 1958, 4 (2), 8-11.—Protein is quant. pptd. from serum with a suitable reagent, the ppt. is dissolved in NaOH soln. and the protein is determined by means of the biuret reaction, the intensity of the colour being measured in a Pulfrich photometer with S53 filter. If the serum shows more than a slight opalescence, the ppt. must be washed first with boiling ethanol and then with ether to remove lipids. Results agree with those obtained by the Kjeldahl method. E. HAYES

308. Constant albumin factor for the calculation of the percentage composition of the serum-protein fraction obtained by elution of paper-electrophoresis strips. O. Meulemans and E. Oosterwoud (Lab. of "Wilhemina Kinderziekenhuis," Utrecht, The Netherlands). *Clin. Chim. Acta*, 1958, 3 (3), 275-279 (in English). H. F. W. KIRKPATRICK

309. Phosphorescence in liquid scintillation counting of proteins. R. J. Hererg (Lilly Res. Lab., Indianapolis, Ind., U.S.A.). *Science*, 1958, 128, 199-200.—Hyamine 10X (*p*-diisobutylcresoxymethoxyethylmethylbenzylammonium chloride) soln. of proteins containing relatively large amounts of material exhibit a phosphorescence phenomenon that interferes with the counting. Elimination of the effect may be achieved by purifying the hyamine by repeated crystallisation from toluene, and by acidification before counting. H. F. W. KIRKPATRICK

310. Assessment of a new simple colorimetric test for proteinuria. D. N. Baron and F. Newman (Royal Free Hosp., London). *Brit. Med. J.*, 1958, 980-981.—Trial of a paper-strip supplied commercially is described. The paper, impregnated with bromophenol blue buffered to pH 3 with citrate and dried, shows a colour change from yellow through green to blue when dipped into urine containing protein. The limit of sensitivity is 5 mg of protein per 100 ml of urine; with concn. of 30 mg or more per 100 ml colour changes are specific for protein and the test is approx. quant. over the concn. range 50 to 300 mg per 100 ml. Slight false positive colours were given occasionally with protein-free urines. H. F. W. KIRKPATRICK

311. Laboratory trial of a paper-strip test for proteinuria. S. C. Frazer (Dept. of Clin. Chem., Royal Infirmary, Edinburgh, Scotland). *Brit. Med. J.*, 1958, 981-983.—The test (*cf.* Baron and Newman, *Anal. Abstr.*, 1959, 6, 310) is less sensitive than present tests, but is adequate for routine use.

Urine preserved with acid or toluene, or stale urines that have undergone alkaline fermentation, are unsuitable for the test. Within the physiological range of urine pH, results are consistent, but semi-quant. interpretation of results may be misleading.

H. F. W. KIRKPATRICK

**312. Method for the separation of nucleotides by concave gradient elution.** H. G. Pontis and N. L. Blumson (King's Coll., Durham Univ., Newcastle upon Tyne, England). *Biochim. Biophys. Acta*, 1958, **27** (3), 618-624.—Separation of most of the mono-, di- and tri-phosphates of adenosine, guanosine, cytidine and uridine as well as the sugar-containing nucleotides is attained by chromatography on Dowex-1 (2 or 4% cross-linked) resin. Elution is with dil. aq.  $\text{CaCl}_2$ -HCl mixtures such that the pH decreases and the  $\text{Cl}^-$  content increases in concave manner during elution. The separation is followed by measuring the extinction of the eluate at 260  $\mu$ ; fractions composing each peak are mixed, the pH is adjusted to 7 with  $\text{Ca}(\text{OH})_2$  in aq. suspension and the neutral soln. is freeze-dried. The  $\text{CaCl}_2$  is removed by washing the residues with ethanol-ether (1:1) and the dried calcium salt of the nucleotide is decomposed in aq. soln. with ammonium oxalate. The purified residues are examined by paper chromatography or other appropriate methods. Recovery varies from 85 to 100%.

W. H. C. SHAW

**313. Improved method for the determination of free and total cholesterol using the ferric chloride reaction.** N. Crawford (Queen Elizabeth Hosp., Birmingham, England). *Clin. Chim. Acta*, 1958, **3** (4), 357-367.—Modifications of previous methods in which this reaction is used are proposed. Extraction is made with Bloor's reagent at room temp.; peak colour production is obtained by the use of a reagent containing 1 mg per ml of  $\text{FeCl}_3$  and deterioration on storage that occurs with a mixed reagent is avoided by adding the  $\text{FeCl}_3$  and  $\text{H}_2\text{SO}_4$  separately.

H. F. W. KIRKPATRICK

**314. New method of determination of cholesterol bound to  $\alpha$ - and  $\beta$ -lipoproteins in serum.** M. Burstein and J. Samaille (Nat. Centre for Blood Transfusion, Paris). *Clin. Chim. Acta*, 1958, **3** (4), 320-327.—Treatment of the serum with  $\text{CaCl}_2$  and dextran sulphate precipitates the  $\beta$ -lipoproteins leaving the  $\alpha$ -fraction in soln. Determination of cholesterol before and after pptn. gives the total and  $\alpha$ -fraction, respectively; the  $\beta$ -fraction is then given by difference.

H. F. W. KIRKPATRICK

**315. High-frequency technique for continuous recording in chromatographic analysis of bile acids.** G. Johansson, K. J. Kärman and A. Norman (Dept. of Anal. Chem., Univ. of Lund, Sweden). *Anal. Chem.*, 1958, **30** (8), 1397-1400.—A special type of cell is described that enables changes in conductivity to be recorded as a function of time during passage of eluates. Application of the apparatus to the separation of free and conjugated bile acids is described.

H. F. W. KIRKPATRICK

**316. Chromatographic method for the quantitative determination of oestradiol, oestrone and oestriol in the urine of non-pregnant women.** E. A. Kakushkina and V. G. Orlova. *Lab. Delo*, 1958, **4** (2), 11-16.—An extract containing the three oestrogens (= 500 ml of urine) is dissolved in benzene-methanol (98:2, w/w) and poured on to a chromatographic column (100 mm  $\times$  10 mm) containing 3 g

of alumina (prepared by heating chromatographic alumina for 2 hr. on a hot-plate and cooling in a desiccator over dry technical alumina), previously moistened with 3 ml of benzene. The column is developed with 2 ml of benzene. Oestrone is then eluted with 15 ml of benzene-methanol (98:2), oestradiol with 10 ml of benzene-methanol (95:5) and oestriol with 10 ml of benzene-methanol (70:30). The eluate is collected in 3-3-ml fractions. The fractions are evaporated to dryness and the oestrogens are determined by the method of Cohen and Bates (*Clin. Endocrinol.*, 1947, **7**, 701).

E. HAYES

**317. Colorimetric determination of oestrone and  $\alpha$ -oestradiol coupled with diazobenzene-*p*-sulphonyl chloride.** E. Rota (Turin Univ., Italy). *Ric. Sci.*, 1958, **28** (3), 566-569.—The optimum conditions for the colorimetric determination of oestrone and  $\alpha$ -oestradiol after coupling with diazobenzene-*p*-sulphonyl chloride have been established. Measurement is made with a 510- $\mu$  filter (green), and a calibration graph for quantities of 5 to 400  $\mu$ g is given; both compounds form derivatives of equivalent colour intensity.

L. A. O'NEILL

**318. Paper-chromatographic method for the measurement of pregnanediol in urine.** W. B. Eberlein, A. M. Bongiovanni and C. M. Francis (Children's Hosp. of Philadelphia, Pa., U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1958, **18** (3), 300-309.—Urine is hydrolysed with glucuronidase and extracted with benzene. The pregnanediol is separated by ascending chromatography, then eluted and determined spectrophotometrically by the reaction with  $\text{H}_2\text{SO}_4$  previously treated with  $\text{NaHSO}_4$ .

H. F. W. KIRKPATRICK

**319. Determination of steroid alcohols with  $^{14}\text{C}$ acetic anhydride.** V. P. Hollander and J. Vinecour (Univ. of Virginia, Sch. of Med., Charlottesville, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1429-1431.—The preparation of the radioactive acetic anhydride is described, and a method given for its application to the determination of 0.2 to 3  $\mu$ g of cortisone by acetylation followed by paper chromatography. Application of the method to mixtures of steroids is also discussed.

H. F. W. KIRKPATRICK

**320. Estimation of small amounts of corticosterone in rat plasma.** N. Zenker and D. E. Bernstein (Dept. of Path. and Med., Mt. Zion Hosp., San Francisco, Calif., U.S.A.). *J. Biol. Chem.*, 1958, **231** (2), 695-701.—The fluorimetric method described is very sensitive and needs only 0.2 ml of plasma for duplicate determinations. The double-extraction technique of Silber and Porter (*Anal. Abstr.*, 1955, **2**, 142) is used together with a modification of the fluorescence technique of Sweat (*Anal. Abstr.*, 1954, **1**, 1944). Other than corticosterone, only cortisol and oestradiol give any fluorescence and this is much less than that given by corticosterone.

J. N. ASHLEY

**321. Bovine blood trans- $\alpha$ -glucosylase, properties and measurement.** K. D. Miller and W. H. Copeland (Div. of Lab. & Res., N.Y. State Dept. of Health, Albany, N.Y., U.S.A.). *J. Biol. Chem.*, 1958, **231** (2), 997-1008.—Methods are described for the determination of trans- $\alpha$ -glucosylase activity in (a) the amylose reaction, and (b) the maltose reaction. The amylose reaction is carried out at pH 7.2 and 37° in a medium that contains the enzyme,

1% of amylose and 0.03 M  $\text{CaCl}_2$ . The glucose produced is determined by a manometric method. The maltose reaction, by which maltose is converted into higher oligosaccharides by transglucosylation, is effected at pH 6.0 and 37° in the presence of 0.015 M maltose. The reaction is studied by methods similar to those used by Monod and Torriani (*Ann. Inst. Pasteur*, 1950, **78**, 65) for *Escherichia coli* amylomaltase. These superimpose the glucose oxidase and catalase systems on the experimental reaction with a subsequent manometric analysis of the glucose produced.

J. N. ASHLEY

**322. The esterase activity of the fibrinolytic system. [Determination of plasminogen.]** M. Lassen (Biol. Inst. of Carlsberg Foundation, Copenhagen, Denmark). *Biochem. J.*, 1958, **69** (3), 360-366.—A method is described for the determination of plasmin (fibrinolysin); it is based on the esterase activity of the enzyme, with benzoyl-L-arginine ethyl ester or L-lysine ethyl ester as substrate. The reaction is carried out in the presence of  $\text{NaHCO}_3$  and the  $\text{CO}_2$  produced is measured in the Warburg apparatus. Conditions are given under which the amount of substrate hydrolysed, and hence the amount of  $\text{CO}_2$  evolved, is proportional to the concn. of plasmin. This method is the basis of a procedure for the determination of human plasminogen in the presence of plasmin inhibitors. Two other facts are of importance—(i) the inhibitors present in the agent (streptokinase) used to activate the plasminogen are ineffective in the proposed method, and (ii) a prep. of human plasmin in which no activator and probably no inhibitors are present is readily made by heating human globulin activated by streptokinase to 100° at pH 2. The determination of plasminogen in plasma is carried out as follows. The plasminogen is converted into plasmin by addition of an excess of streptokinase and the resulting plasmin activity is determined. Increasing amounts of the human plasmin prep. (obtained by heat treatment) are added to plasma and the resulting activities are determined. The mixture of plasmin and plasma, which has the same activity as plasma activated by streptokinase, also contains the same amount of plasmin. A final determination of plasmin in the heated prep. enables the concn. of plasminogen in plasma to be calculated in terms of  $\mu\text{l}$  of  $\text{CO}_2$  per min. per ml of plasma.

J. N. ASHLEY

**323. Manometric studies of bracken [*Pteridium aquilinum* (L.) Kuhn] thiaminase. [Determination of thiaminase activity.]** R. H. Kenten (Biochem. Dept., Rothamsted Exp. Sta., Harpenden, Herts., England). *Biochem. J.*, 1958, **69** (3), 439-448.—Thiaminase catalyses the fission of the bond between the methylene group and the quaternary N of thiamine with transfer of the pyrimidine moiety to an acceptor amine (such as aniline, piperidine, pyridine or trimethylamine) and liberation of  $\text{H}^+$ ; if the reaction is carried out in the presence of  $\text{NaHCO}_3$ ,  $\text{CO}_2$  is liberated and can be determined manometrically. Conditions are described under which the rate of evolution of  $\text{CO}_2$  is proportional to the amount of thiaminase present in the reaction mixture.

J. N. ASHLEY

See also Abstracts—38, Determination of Cu in biological materials. 54, Determination of Ca in the presence of Mg. 113, Determination of  $\text{NH}_4^+$  by formaldehyde method. 116, Determination of

P in biological materials. 133, Determination of  $\text{H}_2\text{S}$  by micro-diffusion. 208, 209, 210, Separation of carbohydrates. 329, 333, Determination of adrenaline and noradrenaline. 334, Determination of rutin. 335, Determination of non-volatile organic acids in biological systems. 344, Determination of betaine. 352, Determination of amylase. 357, Determination of fatty acids. 395, Counter-current distribution: analysis of results. 398, Measurement of O consumption of liver. 408, Indicators for electrophoresis. 427, Determination of redox potential and pH of biological fluids.

#### Pharmaceutical analysis

**324. New reagent for titrations in anhydrous media. I. The determination of codeine, quinine, quinidine and papaverine by means of the hydrochloric acid complex of aluminium chloroisopropylate.** G. Tokár and I. Simonyi (Lab. of the United Pharm. and Foodstuff Factory, Budapest). *Magyar Kém. Foly.*, 1958, **64** (3), 94-96.—The  $\text{HCl}$  complex of aluminium chloroisopropylate (I) acts as a monobasic acid in the formation of salts with various alkalooids and can be used as a soln. in anhyd.  $\text{CHCl}_3$  for titrating alkalooids in an anhyd. medium. The titre of this soln. (0.1 N) changed by only 1 to 2% in 2 months. It is standardised against codeine sulphate. The best indicators are a chlorobenzene soln. of ethyl orange (II) or dimethyl yellow. *Procedure*—Dissolve codeine (0.14 to 0.16 g), quinine or quinidine (0.10 to 0.14 g) or papaverine (0.16 to 0.18 g) in dry  $\text{CHCl}_3$  (5 ml); add a soln. of II (0.2%) (3 to 4 drops) and titrate with I to an orange colour. In the examples given, the error was within  $\pm 1.1\%$ . The ppt. formed during the titration is slightly sol., so that the method is unsuitable for gravimetric determinations.

A. G. PETO

**325. Determination of strychnine and brucine in *nux vomica* seeds, tincture and extract.** R. Fischer and S. Gharbo (Inst. für Pharmakogn., Univ. Graz, Austria). *Pharm. Zentrbl.*, 1958, **97** (3), 101-105.—To determine strychnine (I) and brucine (II) in powdered seeds, mix the alkaline sample with anhyd.  $\text{Na}_2\text{SO}_4$ , place the mixture over a layer of  $\text{Al}_2\text{O}_3$  in an apparatus for continuous extraction and extract with  $\text{CHCl}_3$  for 2 hr. Evaporate the extract to dryness, dissolve the residue in trichloroethylene and apply the soln. to a chromatographic column of  $\text{Al}_2\text{O}_3$  containing 5% of  $\text{H}_2\text{O}$ . Develop with a 0.5% soln. of acetone in trichloroethylene and pass the eluate through a second column which contains  $\text{H}_2\text{O}$ -free  $\text{Al}_2\text{O}_3$ . Separately elute II from the first column and I from the second column with methanol, evaporate and titrate. The complete assay takes  $\approx 5$  hr. To assay the tincture, pass the sample through a column of  $\text{Al}_2\text{O}_3$  and elute with methanol. Evaporate the eluate to dryness, dissolve the residue in trichloroethylene and pass through successive columns of  $\text{Al}_2\text{O}_3$  containing 10% of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$ -free  $\text{Al}_2\text{O}_3$ . Develop with a 1% soln. of acetone in  $\text{CCl}_4$  and complete the determination as above. To assay the extract, treat an alcoholic soln. as described for the tincture, but with  $\text{Al}_2\text{O}_3$  containing 5.5% of  $\text{H}_2\text{O}$  in the first column.

A. R. ROGERS

**326. Analysis of preparations containing ergot.** F. Schlemmer (Dtsch. Arzneiprüfungs-Inst., München). *Pharm. Weekbl.*, 1958, **93** (6), 257-261.—A discussion is presented of the interpretation of the results of established methods of analysis of ergot preparations.

A. R. ROGERS



327. **Arecoline in forensic science.** R. M. Ternikova. *Sb. Nauch. Rabot. Mosk. Farmatsevt. Inst.*, 1957, **1**, 75-84; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,527.—The behaviour of arecoline (I) towards general reagents for alkaloids is studied. The greatest sensitivity of I is towards Dragendorff's reagent ( $\text{KBiI}_4$ ) (1 in  $3 \times 10^4$ ), Sonnenschein's reagent (molybdophosphoric acid) or tungstosilicic acid (1 in  $5 \times 10^4$ ). The formation with  $\text{KBiI}_4$  of complex clusters of orange-red crystals in the form of rhombs and parallelograms is specific.

C. D. KOPKIN

328. **Identification of solanine.** E. G. C. Clarke (Dept. of Physiol., Royal Vet. Coll., London). *Nature*, 1958, **181**, 1152-1153.—A deep steel-blue colour is given by solanine ( $<1 \mu\text{g}$ ) with a 1% soln. of paraformaldehyde in 90%  $\text{H}_3\text{PO}_4$ . The charring often associated with the use of the usual Marquis reagent is avoided. Of the 300 alkaloids tested, only  $\alpha$ -chaconine and solanidine gave an identical colour.

A. R. ROGERS

329. **Fluorimetric determination of adrenaline and noradrenaline in aqueous solution.** S. Roston (Dept. of Biochem., U.S. Army Med. Res. Lab., Fort Knox, Ky., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1363-1366.—In the method described, oxidation is first carried out by means of ferricyanide at pH 5-5 to produce adrenochrome and noradrenochrome; the corresponding fluorescent compounds are then formed by separate preferential treatments with NaOH and ascorbic acid. By this means the determination of either substance is largely independent of the concn. of the other. The method is highly specific.

H. F. W. KIRKPATRICK

330. **Investigation of the constituents of *Digitalis purpurea*.** K. J. Harkiss and G. J. Rigby (Dept. of Pharm., Univ. Manchester, England). *J. Pharm. Pharmacol.*, 1958, **10** (4), 228-236.—Increase in the concn. of ethanol, or the inclusion of methanol, ethanediol or glycerol in the alkaline 3:5-dinitrobenzoic acid assay for digitalis glycosides progressively reduces the max. extinction of the reaction mixture. The concn. of deacetyldigilanes A and B, digitoxin and gitoxin in samples of powdered *D. purpurea* leaf have been determined by chromatographic separation and chemical assay. The total biological activity of a sample estimated as the sum of the activities represented by each of the four glycosides determined chemically is about half that estimated by direct biological assay. Possible causes of the discrepancy are discussed. **Procedure**—Decolorise a tincture (containing the extractive from 225 mg of leaf) by passage through a column of  $\text{Al}_2\text{O}_3$ , transfer quant. to a strip of filter-paper and develop with a satd. soln. of ethanediol in  $\text{CHCl}_3$  by the method of Rigby and Bellis (*cf. Anal. Abstr.*, 1957, **4**, 246). Elute each glycoside separately with 70% ethanol or with  $\text{CHCl}_3$ -methanol (1:1), evaporate the extract under reduced pressure, dissolve the residue in ethanol (5 ml),  $\text{H}_2\text{O}$  (2 ml) and 2% ethanolic 3:5-dinitrobenzoic acid (2 ml), add *N* NaOH (1 ml), filter through sintered glass and measure the extinction at 535  $m\mu$  at 1-min. intervals until the max. is reached. Apply "blank" corrections and calculate by reference to a calibration curve.

A. R. ROGERS

331. **Counter-current separation of constituents of *Digitalis purpurea*.** K. J. Harkiss and G. J. Rigby (Dept. of Pharm., Univ. Manchester, England). *J. Pharm. Pharmacol.*, 1958, **10** (4), 237-241.—

Mixtures of deacetyldigilanes A (I) and B (II), digitoxin (III) and gitoxin (IV) have been partitioned in the system ethyl acetate - benzene -  $\text{H}_2\text{O}$  (43:7:25) by counter-current distribution. I and II are separated from each other and from III and IV by distribution in 49 stages, but separation of III from IV is not achieved.

A. R. ROGERS

332. **Digitalis glycosides. I. Quantitative determination of mixtures of digitalis glycosides by paper chromatography.** L. Fuchs, M. Wichtl and H. Jachs (Pharmacog. Inst., Vienna Univ.). *Arch. Pharm., Berlin*, 1958, **291** (4), 193-208.—The determination is carried out with an alkaline soln. of picric acid as developer. Examples are given of the determination of digilanes A, B and C, strosposide, acetyldigitoxin, acetyldigoxin, digoxin, digitoxigenin, gitoxigenin, and of the more soluble glycosides in *Digitalis lanata* leaves; also of purpurea glycosides A and B, glucogitaloxin, strosposide, verodoxin, gitaloxin, digitoxin, gitoxin, digitoxigenin, and of the more soluble glycosides in *Digitalis purpurea* leaves.

M. H. SAWISTOWSKA

333. **Effect of light on fluorescence of ethylenediamine derivatives of adrenaline and noradrenaline.** A. Goldfien and R. Karler (Dept. of Physiol., Univ. of Calif., San Francisco, U.S.A.). *Science*, 1958, **127**, 1292-1293.—The differences in the published curves of Mangan and Mason (*Anal. Abstr.*, 1958, **5**, 1612) and those of Persky and Roston (*Science*, 1955, **118**, 381) are related to quant. or qual. differences, or both, in the exposure to light. It is also shown that exclusion of blue and u.v. light results in an emission spectrum differing from the previously published findings.

H. F. W. KIRKPATRICK

334. **Colorimetric determination of rutin with uranyl salts.** T. Bross and U. Bilińska (Inst. of Inorg. Chem., Wrocław, Poland). *Acta Polon. Pharm.*, 1958, **15** (1), 39-43.—The concn. of rutin in alcoholic extracts is determined absorptiometrically by measuring the intensity of the colour of an orange complex formed by rutin and uranyl acetate. The maximum extinction is obtained with equimolar soln. in a 1:1 ratio. This method compares favourably with Job's method, and concn. in the p.p.m. range can be determined.

H. DMOWSKA

335. **Analysis of the non-volatile acids in cigarette smoke by gas chromatography of their methyl esters.** L. D. Quin and M. E. Hobbs (Duke Univ., Durham, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1400-1405.—In this method, which could be extended to the analysis of non-volatile organic acids in biological systems, the acids are converted into their methyl esters with diazomethane before chromatography. Lactic, glycolic, succinic and malonic acids comprise 75% of the total content of the non-volatile acid fraction of cigarette smoke.

K. A. PROCTOR

336. **The non-aqueous titration of sulphonamides with perchloric acid.** J. Meulenhoff (N.V. Nederlandsche Combinatie voor Chemische Industrie, Amsterdam). *Pharm. Weekbl.*, 1958, **93** (6), 262-267.—Directions are given for the non-aqueous titration of *p*-aminobenzoic acid, ethyl *p*-aminobenzoate, anthranilic acid and 12 sulphonamides. The procedure with most samples is to dissolve the sample in glacial acetic acid, precipitate the perchlorate of the base with excess of a soln. of  $\text{HClO}_4$  in acetic acid in the presence of benzene,  $\text{CCl}_4$  or

$\text{CHCl}_3$  or a mixture of  $\text{CHCl}_3$  and  $\text{CCl}_4$ , and back-titrate after an interval of 30 min., with 1-naphtholbenzene in benzene as indicator. A. R. ROGERS

**337. Colorimetric determination of organic nitro compounds used as vasodilators.** F. J. Bandelin and R. E. Pankratz (Flint, Eaton and Co., Decatur, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1435-1437. —The nitro compound (about 100 mg) is first removed from the sugar or mannitol diluent by extraction with  $\text{CHCl}_3$  or acetone. After evaporation of the solvent under reduced pressure the residue is dissolved in glacial acetic acid (2 ml), diluted to 100 ml with iron reagent (0.05%  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  soln. in 75% v/v  $\text{H}_2\text{SO}_4$ ), 5 mg of  $\text{Na}_2\text{SO}_3$  is added as an accelerator and the colour is read at 510 m $\mu$ . Potassium nitrate is used as a primary standard.

H. F. W. KIRKPATRICK

**338. Quantitative determination of piperazine salts.** H. Bandel [Caixa Postal 18,026 (Aeroporto), Sao Paulo, Brazil]. *Dtsch. ApothZig*, 1958, **98** (3), 61-62. —Piperazine (I) (e.g., in anthelmintic prep.) is determined gravimetrically as the reineckate. Dissolve the sample containing  $\approx 100$  mg of I hexahydrate in 50 ml of water and 0.25 g of citric acid. Add over 2 to 3 min. 50 ml of freshly prepared satd. aq. ammonium reineckate soln. ( $\approx 3\%$ ) (II) through a capillary jet via the walls of the beaker, mix by careful swirling. Filter after 1 hr., wash the ppt. three times with 10 ml of diluted II (1:500), dry for 2 hr. at 100° and weigh as  $\text{C}_4\text{H}_{10}\text{N}_2 \cdot \text{HC}(\text{NH}_2)_2(\text{SCN})_2$ . Results are accurate to within  $\pm 0.3\%$ .

A. G. COOPER

**339. Chromatographic analysis of Xeroform [bis-muth tribromophenoxide].** A. Castiglioni (Inst. für Warenkunde, Univ., Turin). *Z. anal. Chem.*, 1958, **161** (1), 40-42. —Basic bismuth gallate and free tribromophenol can be detected in small samples of bismuth tribromophenoxide by the simultaneous ascending chromatography of a neutral ethanolic suspension of one portion of the sample and an acidified ethanolic soln. of another portion. The two spots are placed side by side and developed with butanol saturated with  $\text{H}_2\text{O}$ . After 2 hr. the chromatogram is treated with aq.  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$  soln. at about half-way between the origin and the front and  $\text{AgNO}_3$  soln. applied close to the front. The presence of tribromophenol is shown by an orange fleck with  $\text{AgNO}_3$  on the neutral chromatogram and basic bismuth gallate by a blue-black spot with  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$  on the acid chromatogram. An orange fleck on the acid chromatogram is due to the acid decomposition of the bismuth tribromophenoxide.

G. BURGER

**340. Analysis of pharmaceutical tablets by X-ray diffraction spectrometry.** L. Molle (Lab. de Chim. Anal. et Toxicol., l'Univ. Libre de Bruxelles). *Pharm. Weekbl.*, 1958, **93** (7), 334-341 (in French). —Compressed tablets of bismuth subnitrate, KI, KBr and sulphonamides have been examined by X-ray diffraction spectrometry with Cu  $K_\alpha$  radiation of 1.542 Å. The method can be used for rapid qualitative identification, and in favourable cases for semi-quantitative determination in mixtures.

A. R. ROGERS

See also Abstracts—207, 355, Determination of water in glycerol. 243, Chromatography of N-substituted phenothiazines. 279, Determination of meprobamate in urine. 280, Determination of bemegride in blood. 292, Determination of quercetin in rutin. 399, Apparatus for bio-assays.

## Food

*Foods and food additives, beverages, edible oils and fats, vitamins.*

**341. Determination of iron [in food products].** N. M. Rusin and V. F. Rabinovich. *Inform. Byull. Mosk. Nauch. Inst. Sanit. i Gigieny*, 1957, (10-11), 66-67; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,401. —A variation of the visual colorimetric determination of Fe in food products as the thiocyanate complex is described. Ignite 5 to 10 g of the substance to be analysed, evaporate the ash twice with 5 ml of 10% HCl, dissolve the dry residue in water and make up to 50 ml. Filter 5 or 10 ml of the resulting soln. into a cylinder, add water (50 ml), HCl (sp. gr. 1.19, 1 ml) and 30%  $\text{H}_2\text{O}_2$  (3 or 5 drops), mix, add 50%  $\text{NH}_4\text{SCN}$  (or KSCN) soln. (2 ml) and make up to 100 ml. Compare the colour of the soln. with that of a standard soln. of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ . In the presence of  $\text{PO}_4^{3-}$ , extract the coloured iron complex with diethyl ether and complete the determination by colorimetric titration.

C. D. KOPKIN

**342. Determination of sugar in sugar beets. III; IV.** W. H. Parker. *Int. Sugar J.*, 1958, **60**, 159-161; 197-200. —A reference hot-water digestion method for the analysis of the sugar in brei has been developed. The method is based on that of Sachs and le Dichte. Most of the sugar in a normal aliquot of brei is leached out with hot water in a specially designed diffuser. When  $\approx 200$  ml of the diffused juice has been collected in a 200-ml flask, the contents are made up to volume and polarised. The exhausted brei contains  $\approx 5\%$  of its original sugar and is further extracted. The juice is collected in a second flask, made up to volume, and polarised. The sum of the two polarisations gives the pol of the brei. The errors due to marc volume and transfer of brei are negligible as they have only 5% of the effect of the equivalent errors in the single-extraction method. The reference method gave results consistently higher than those of the single hot-water digestion method; this difference is attributed to variations of marc volume.

D'Orazi's method (cf. *Ind. Saccar. Ital.*, 1952, **45**, 82) of calculating the juice volume from the pols of the brei and the expressed juice is described. The errors introduced by variations in basic lead percentage of total lead of the clarifying reagent are discussed. The pol is shown to decrease with increasing basicity of the reagent; at zero basicity the average pol was 0.09% higher than that with the standard reagent, and at 52.06 basicity the average pol was 0.11% lower. The overall effect of increasing the concn. of the basic Pb acetate is to cause a depression of the pol. Dilution of the reagent causes a slight lowering of the basicity, owing to hydrolysis. Pure sucrose soln. behave in a similar way. Rapid methods of determining the concn. and basicity of the Pb acetate reagent are described. Distilled or demineralised water should be used in auto-pipettes to obviate the formation of a ppt. and hence a volume reduction and raising of the pol.

SUGAR IND. ABSTR.

**343. Modification of the von Stieglitz electro-metric method for sugar titrations.** L. W. Chubb and A. W. Hartley (Spillers Central Lab., Station Rd., Cambridge, England). *Analyst*, 1958, **83**, 311-312. —The method of von Stieglitz for the titration of sugar soln. with Fehling's soln. (*Proc. Queensland Soc. Sugar Cane Technol.*, 1936, 101;

1938, 29; 1939, 43) requires the preparation of a special electrode having a porous plug of plaster of Paris, and the useful life of such an electrode is short. The plug can be replaced by the outer case of a Cambridge pH reference electrode or one of a similar type. This electrode has a ground glass sleeve that allows electrical contact to be maintained between the inside and outside of the electrode. The apparatus is described. Titres agree with those of the Lane and Eynon method to within 0.1 ml in 25 ml. A. O. JONES

**344. Determination of betaine in the form of reineckate.** A. Simenauer (Centre Nat. de la Rech. Sci., Paris, France). *Bull. Soc. Chim. France*, 1958, (3), 294-297.—A procedure for the purification of betaine reineckate, prepared for the determination of betaine in sugar beet, is described. The ppt. containing 2 to 20 mg of betaine is dissolved in 5 ml of aq. acetone, and 5 ml of 0.1 N  $\text{AgNO}_3$  is added. The ppt. is centrifuged and washed, and the liquid is boiled to eliminate acetone and treated with 1 ml of aq.  $\text{H}_2\text{SO}_4$  (1:1) and a slight excess of satd.  $\text{KMnO}_4$  soln. After 15 min. on the water bath, excess of  $\text{KMnO}_4$  is destroyed with methanol. A soln. of  $\text{NaCl}$  (30%) (1 ml) is added and, after filtering, the pure reineckate may be re-pptd. in the filtrate. Other possibilities for the separation of the reineckates of other bases from the ppt. are discussed. Gravimetric determination of betaine as reineckate is considered unsatisfactory. Colorimetric determination is discussed. The aq. acetone solution of the reineckate obeys Beer's law, but impurities which may be present cause errors. The molar extinction of ammonium reineckate is considerably less than that of betaine reineckate or choline reineckate, and standardisation must be effected with the base to be determined. Volumetric methods of determination by several authors are reviewed. E. J. H. BIRCH

**345. Determination of dry substance in molasses and massecuites.** E. T. Relf. *Proc. Queensland Soc. Sugar Cane Technol.*, 25th Conf., 1958, 189-193.—The drying of molasses samples in a vacuum oven at 60° to 63° gave reliable results, whereas air-oven drying at 105° gave variable results. The methods of drying with sand or with neutral filter-paper strips (Josse method), as recommended by the 10th Session of I.C.U.M.S.A. (*cf. Int. Sugar J.*, 1950, 52, 243) were compared. Samples of diluted molasses or massecuites were dried *in vacuo* at 60° to 63° for various periods of time. Moisture differences between samples heated for 24 and 44 hr. were <1 mg with the Josse method and 11.7 mg with the sand method. Adequate dispersion of samples is essential and the use of 550 sq. cm of filter-paper (both sides) for 1 g of sample with 1.5 ml of water is recommended. Both sucrose and glucose were stable for 72 hr. of heating *in vacuo* at 60° to 63°. It is therefore concluded that weight losses in molasses that have been dried for long periods are the result of deterioration of non-sugars and their effect on sucrose and reducing sugars. SUGAR IND. ABSTR.

**346. The detection of polyoxyethylene compounds used as crumb softeners in bread.** R. Kliffmüller (Staatl. Chem. Untersuchungsamt, Giessen, Germany). *Dtsch. LebensmittlRdsch.*, 1958, 54 (3), 59-61.—The method is a modification of the paper-chromatographic method of Jaminet (*J. Pharm. Belg.*, 1954, 9, 318). *Procedure*—Dried bread crumbs (10 g) are extracted on the water bath with

96% ethanol (2 × 20 ml), filtered, and evaporated to dryness. The residue is dissolved in ethanol and applied to a chromatography paper together with a control extract and standards, e.g., soln. of polyethylene glycol-400 monostearate (**I**), and Tween 60. The development solvent is made from 50 ml of *n*-butanol, 25 ml of aq.  $\text{NH}_3$  (1:10) and 12 ml of ethanol. The developed chromatogram is dried and sprayed with either ammonium cobalt thiocyanate reagent [17.4 g of  $\text{NH}_4\text{SCN}$  and 2.8 g of  $\text{Co}(\text{NO}_3)_2$  dissolved in 100 ml of water] or, preferably, a modified Dragendorff reagent (850 mg of bismuth subnitrate dissolved in 10 ml of glacial acetic acid and 40 ml of water, mixed with 8 g of KI in 20 ml of water, kept in the dark and diluted 1:12 with 20% acetic acid before use). **I** gives two spots of  $R_f$  values 0.95 to 0.98 and 0.63 to 0.68, both of which are reproduced in extracts of bread baked with 0.5% and 2% of **I**. An extract of a control bread gave one diffuse spot at  $R_f$  0.8 to 0.95. The detection of 2% of **I** in bread was also made by dissolving the extract, freed from alcohol, in 1 ml of normal saline and mixing 0.1 ml with 0.1 ml of a fresh suspension of blood corpuscles. Haemolysis was produced in 16 hr.; extracts of a control loaf and bread baked with 0.5% of **I** gave a negative response. E. C. APLING

**347. Determination of starch in sausage meat and calculation of the nitrogen correction for cereal content.** J. R. Fraser and D. C. Holmes (Dept. of the Gov. Chemist, Clement's Passage, Strand, London). *Analyst*, 1958, 83, 371-372.—The minced and well-mixed sample (5 g) with 10 ml of water is heated in an autoclave for 10 min. at 15 lb per sq. in. with 50 ml of acidified  $\text{CaCl}_2$  soln. (an aq. soln. containing  $\text{CaCl}_2$  and Na acetate, adjusted to pH 2.3 with acetic acid and to a sp. gr. of 1.3 at 20°). The diluted soln. is clarified with Zn acetate and  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. and adjusted to 100 ml with the  $\text{CaCl}_2$  soln. After filtration, and discarding of the first 15 to 20 ml of filtrate, the optical rotation of the clear filtrate is determined and the amount of starch present is calculated ( $[\alpha]_D^{20} = 200$ ). The amount of N associated with this amount of starch is found by multiplying the starch content by 0.025. The total content of N of the sample is then corrected for this amount of N and the corrected figure is related to the lean meat content by means of the usual factors (100/3.4 for beef and 100/3.6 for pork). The method serves as a useful check on other methods and as a simple routine method. It is not applicable without modification when other fillers such as soya flour or dried milk are present. A. O. JONES

**348. Methods for sampling milk and milk products.** British Standards Institution (2 Park St., London, W.1). Amendment PD 3005 to B.S. 809:1949, 1958, 4 pp.—This amendment extends the range of sampling methods for dairy products to include the sampling of ice-cream, water ices and similar frozen confections. N. E.

**349. The aminocarbonyl reaction of milk products. X. Colorimetric determination of hydroxymethylene-glycolaldehyde.** Susumu Adachi (Lab. of Animal Products Technol., Fac. Agric., Tohoku Univ., Kita-rokubancho, Sendai). *J. Agric. Chem. Soc. Japan*, 1957, 31 (2), 93-97.—Folin's reagent (**I**) yields a blue colour (a faint peak at 875  $\mu\mu$ ) with hydroxymethyleneglycolaldehyde in a phosphate buffer of pH 6.2. The extinction becomes constant

by heating the soln. in a boiling-water bath for 3 min. and remains unchanged for >2 hr. in sunshine. The working curve (at 730 m $\mu$ ) is linear for 5 to 240  $\mu$ g per 4 min. Cystine, glutathione and ascorbic acid give a similar coloration, but the action of the first two compounds is inhibited with iodoacetamide soln. (18.6%, 0.1 ml) and that of the last compound with CuSO<sub>4</sub> soln. (0.025%, 0.1 ml). Van Slyke-Hawkin's tungstophosphoric acid soln. (9 ml for 1 ml of the sample) is the best deproteinising agent. The deproteinised sample (2 ml) is mixed with the inhibitors, phosphate buffer (1 ml) and I (0.5 ml), diluted to 4 ml, heated and determined photometrically.

K. SAITO

**350. Chlorine-containing extraction-medium residues in caffeine-free coffee. Micro-method for the determination of halogenated hydrocarbons. The behaviour of the solvent residues in caffeine-free coffee.** H. Hadorn and H. Suter (VSK Lab., Basle). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (3), 141-165.—Various methods for determining the amount of chlorinated hydrocarbon solvent remaining in caffeine-free coffee after extraction of caffeine are critically reviewed. The combustion method of Deshusses and Desbaumes (*cf. Brit. Abstr. C*, 1950, 501) has been modified to give satisfactory results for 50 to 100  $\mu$ g of chloride. The solvent residues are removed by treatment of the sample with purified air and steam under reflux and the vapours decomposed in a red-hot quartz tube. The combustion gases are absorbed in an alkaline soln. (1% NaOH soln. with 0.3% of As<sub>2</sub>O<sub>3</sub>), the chloride being pptd. as silver chloride. This ppt. is filtered off and converted into metallic silver, which is dissolved in HNO<sub>3</sub> and titrated with dithizone. Experimental details are given, and results obtained for various commercial caffeine-free coffees are discussed. No conclusive information could be obtained on the amount of solvent removed by roasting, but considerable quantities remain in roasted beans, some of which is given up on grinding or storing in the open. Of that remaining, 10 to 15% is carried over into the infused coffee drink.

S. M. MARSH

**351. Determination of the oxygen content of air in beer by gas-solid chromatography.** J. L. Bethune and F. L. Rigby (Canadian Breweries Res. Div., Toronto). *J. Inst. Brewing*, 1958, **64** (2), 170-175.—It is shown that the collection of air from beer in a conventional apparatus is unsatisfactory, since O is absorbed by a mixture of beer and alkali during removal of CO<sub>2</sub>. An apparatus is illustrated in which the air from the beer package is collected over mercury, and any beer carried over is removed before the gas is transferred to the burette for measurement and removal of CO<sub>2</sub>. From the burette the residual gas is passed to the chromatography column. This consists of a tube (10 ft.  $\times$  6 mm), packed with Molecular Sieve Type 5A (30 to 60 mesh) and activated by heating *in vacuo* at 180° for 24 hr. The separation is run at 103° with 28 ml per min. of He as carrier gas, detection being by a thermal conductivity cell and recorder. The proportion of O is obtained by measurement of the areas under the peaks for O and N. It is noted that A has a retention time comparable with that of O under the given conditions. The proportion of A in the air dissolved in beer is  $\approx$ 1%. Comparison of results by the conventional and the present methods of collection of the air show much less variability with the mercury method. For two series of replicates, the mean vol. of air and its O

content with collection over mercury were 3.3 ml and 10 to 12% and 2.1 ml and 8 to 9%, respectively, the corresponding figures with conventional collection being 2.9 ml and 2 to 12% and 1.9 ml and 2 to 7%.

R. E. ESSERY

**352. Measurement of enzymatic amylolytic activity. Group B. II. Methods depending on the biological evaluation of decomposition products of starch.** H. Wildner and G. Wildner (Ireks Forschungsinstit. für Gärungswissenschaft, Kulmbach, Germany). *Brauwissenschaft*, 1958, **11** (3), 59-65.—Appropriate procedures are discussed for determining diastatic activity by measurement of the amount of ethanol or CO<sub>2</sub> formed by the fermentation of the hydrolytic products of starch. A modified procedure for Foth's method for determining the yield of ethanol from starchy material, and a selective fermentation method for the determination of glucose together with maltose, are described.

P. S. ARUP

**353. Investigation and determination of benzoic acid and p-hydroxybenzoic acid in wine.** T. Eschena (Ist. di Chim. Agrar., Univ. of Perugia, Italy). *Ann. Sper. Agrar.*, 1957, **11**, 1301-1310.—These preservatives are determined qual. and quant. by coupling the diazo derivatives with N-1-naphthylethylenediamine. Interference from aromatic compounds present in wines is eliminated by an extraction and dilution procedure. *Procedure*—Extract the sample (5 ml) with a mixture of acetone (5 ml) and ether (5 ml), then twice with ether (5 ml). Wash the extract with water (3 ml), then extract twice with a 1% soln. of NaHCO<sub>3</sub> (3 ml). Transfer the extracts to a 25-ml flask, add 95% ethanol (10 ml) and acetone (5 ml) then make up to vol. with 95% ethanol. To determine benzoic acid, transfer an aliquot (5 ml) of this soln. to a dish, add 1 drop of a 30% soln. of NaOH and evaporate the solvents on a water bath. Add a nitrating mixture (2 ml) (prep. described), heat on a water bath for 45 min., add water (20 ml) and a 30% soln. of NaOH (5 ml), and transfer to a separator. Extract with ether (30 ml), discard the water phase and extract the organic phase twice with a 3% soln. of NaOH (5 ml). Add conc. HCl (1 ml) and reduce the nitro compound with zinc (2 g) for 10 min. Transfer the soln. to a 25-ml flask, add a 2.5% soln. of NaNO<sub>2</sub> (1 ml), allow to stand for 10 min., add a 5% soln. of ammonium sulphamate (2 ml) and set aside for 10 min., with occasional shaking. Add a 1% soln. of N-1-naphthylethylenediamine hydrochloride (prep. described), and after 10 min. measure the extinction at 540 m $\mu$ , against a blank; refer the result to a calibration curve. Salicylic acid and p-hydroxybenzoic acid do not interfere. To determine p-hydroxybenzoic acid, carry out the nitration on another aliquot at room temp. for 30 min. then proceed as described above. A simplified qual. test can be used for detecting up to 50 mg of preservative per litre. Quant. recovery tests gave a precision within  $\pm$ 10%.

R. LACERNA

**354. Routine control method for determining the ratio of malic acid to lactic acid in wine.** H. Tanner and H. Rentschler (Eidg. Versuchsanstalt f. Obst-, Wein- u. Gartenbau, Wädenswil, Switzerland). *Mitt. Wein- u. Obstbau, Wien*, A, 1958, **8** (3), 113-120.—The samples are first freed from cations by shaking with a little Dowex-50 resin, and then tested by a paper-chromatographic procedure with the use of an ascending solvent composed of n-butanol, isobutyl alcohol and tert.-amyl alcohol (1 + 1 + 1)



(30 ml) in admixture with 15 ml of a soln. containing formic acid (50 ml), acetic acid (150 ml), water (200 ml) and bromophenol blue (1 g). Several samples are tested on the same chromatogram in parallel with an aq. standard soln. containing malic acid (0.5%), tartaric acid (0.5%) and 90% lactic acid (0.55%). After air-drying, the chromatogram shows separate spots (yellow on a dark-blue background) for the three above-mentioned acids, the intensity and dimensions of which afford a rough indication of the progress of the conversion of malic into lactic acid, and also a check on the content of tartaric acid. P. S. ARUP

**355. Determination of water in glycerol, margarine, oils and fats.** C. B. Stuffs (Anal. Dept., J. Bibby & Sons Ltd., Gt. Howard St., Liverpool, England). *Analyst*, 1958, **83**, 312-314.—The apparatus described is a modification of that of Heidbrink (*Fette u. Seif.*, 1951, **5**, 291) and consists of two aluminium plates resting in a cradle fitted with a hook from which the upper plate can be suspended. The sample of glycerol (0.35 to 0.45 g) or of margarine, oil or fat (1.75 to 2 g) is placed on the lower plate, the upper plate is placed over the lower and the two are rubbed together. The plates are then placed in the cradle and the apparatus is weighed ( $\approx 20$  g) to within 0.0001 g. It is then placed in a vacuum oven maintained at 58° (70° for margarine, etc.), the top plate is lifted on to the hook and the oven is evacuated (—27 in. of mercury). After 5 hr. for glycerol and 1 hr. for margarine, etc., the upper plate is replaced on the lower, the apparatus is allowed to cool in a desiccator and the loss of wt. is determined. Results for glycerol agree with those found by the Karl Fischer method and by subtracting glycerol plus residue at 160° from 100, and results for margarine agree with those found by the Dean and Stark method. A. O. JONES

**356. Characterisation of semi-drying oils in olive oil.** — Vizern and — Guillot (Vizern and Guillot Anal. Lab., Marseilles). *Chim. Anal.*, 1958, **40** (4), 118-119.—A method described earlier for the characterisation of semi-drying oils in olive oil (*Ann. Falsif.*, 1939, June) is based on the insolubility of certain tetrabromolinoleic glycerides in light petroleum. The method has never given a false indication even with olive oils of high I.V., but pure arachis oils with a similar I.V. gave a ppt. as did a mixture (I.V. 82) of pure olive oil (I.V. 80) with 5% of soya oil (I.V. 120). The ppt. obtained from soya oil contains 47.2% of bromine, in agreement with the calculated figure for the bromide of oleic dilinoleic glyceride (47.62%), but not with the figure for dioleic linoleic glyceride tetrabromide (42%). While pure olive oil gives no ppt. under the test conditions, the fatty acids derived from it do give a ppt. of tetrabromolinoleic acid. Since certain oils contain as much as 50% of free acid, it is possible that errors may arise. A study of mixtures containing known quantities of fatty acids and the oils from which they derive has shown that no ppt. is obtained if the acidity is less than 70%. It is concluded that the method may be applied to oils with high I.V. and high free acid content without risk of error. S. M. MARSH

**357. Paper chromatography of saturated and unsaturated fatty acids.** [Determination of fatty acids.] P. E. Ballance and W. M. Crombie (Dept. of Botany, Univ. of Southampton, England). *Biochem. J.*, 1958, **69** (4), 632-640.—The separation

of more than 40 pure fatty acids on several reversed-phase paper-chromatographic systems is described. For saturated and unsaturated  $C_{12}$  to  $C_{22}$  acids the best system is liquid paraffin and aq. acetic acid. For acids that contain more than 1 hydroxyl group a suitable system is castor oil-aq. acetic acid. The acids may be determined by photometric estimation of the Cu (as the dithio-oxamide complex) retained in the paper by the copper soaps of the fatty acids when the papers are immersed in aq. cupric acetate. One to 70  $\mu$ g of acid in each spot and total amounts of mixed acid up to 140  $\mu$ g can be determined. A method is described for the analysis of mixtures of saturated and unsaturated acids by comparison of the chromatograms of (a) the original mixture, (b) the mixture after hydrogenation, and (c) the mixture after oxidation with alkaline  $KMnO_4$ . For a full analysis, only 5 mg of mixed acids is necessary. J. N. ASHLEY

**358. Paper chromatography of the higher saturated fatty acids.** S. Fiker and V. Hájek (Inst. Hyg., Prague). *Chem. Listy*, 1958, **52** (3), 549-551.—Whatman paper No. 3 (10 cm  $\times$  18 cm) is impregnated with a mixture prepared by dissolving paraffin wax (m.p. 42° to 46°) (5 g) and liquid paraffin ( $d = 0.900$ ) in 100 ml of  $CHCl_3$ -benzene (4:1). Anhyd. acetic acid satd. with paraffin wax and liquid paraffin at 55° or 85° is used as the developing system. The chromatograms are developed by the ascending technique for 2 to 3 hr. at 55° or 85°, then dried and treated for 45 min. with  $AgNO_3$  soln. (5%) at 80°. The chromatograms are washed with water ( $\times 5$ ) and dried for 10 min. at 150°. Brown spots indicate the presence of fatty acids. J. ZÝKA

**359. New partition agent for use in the rapid separation of fatty acid esters by gas-liquid chromatography.** S. R. Lipsky and R. A. Landowne (Yale Univ. Med. Sch., New Haven, Conn., U.S.A.). *Biochim. Biophys. Acta*, 1958, **27** (3), 666-667.—Polyethylene glycol adipate mixed with 4 parts of acid-washed Celite 545 (120 to 140 mesh) is recommended as the partition phase in the separation of fatty acid methyl esters. On a U-shaped glass column (8 ft.  $\times$  6 mm) operated at 186° with He as carrier gas (40 ml per min. at 38 lb per sq. in. pressure), complete elution of a standard ester mixture up to  $C_{22}$  is attained in 85 min. The increased retention times that occur as the degree of unsaturation increases enable each member of the  $C_{18}$  series to be separated from the preceding less-unsaturated member. W. H. C. SHAW

**360. Paper chromatography in the fat field.** XXIV. Further studies on the paper chromatography of fatty acids. H. P. Kaufmann and E. Mohr (Inst. für Pharm. und Lebensmittelchemie, Univ. Münster). *Fette, Seif., Anstrichmitt.*, 1958, **60** (3), 165-177.—The method of Kaufmann and Nitsch (*Anal. Abstr.*, 1955, **2**, 2557; 1956, **3**, 849) is further studied, individual steps being examined experimentally and the results compared with those to be expected theoretically. The essential features of the method do not require modification, but some improvements are suggested. The impregnation of the paper has a marked effect on the separation achieved and on the time of development; standardisation of this step is desirable. The range of application of the hydrocarbon-acid-water solvent system can be extended by the addition of polar compounds to the ascending system; acetone and

methyl cyanide give the best results, greatly reducing the development time and making chromatography at higher temperatures possible. The addition of acetone increases  $R_F$  values and also the  $R_F$  differences of the acids separated. For chromatography at low temperatures, the system undecane-acetone-propionic acid-water gives the best results.

E. HAYES

**361. Loss in  $\beta$ -carotene determination.** Saburo Kitagawa and Atushi Tamura. *Ann. Rep. Nat. Inst. Nutr., Tokyo*, 1957, 62.—Carotene is generally stable in alkaline solution, but, during hot extraction and saponification, increased alkalinity accelerates isomerisation, and causes destruction of  $\beta$ -carotene. Absorption curves (330 to 480 m $\mu$ ) are given for yellow and red pigments produced from synthetic  $\beta$ -carotene during saponification.

M. D. ANDERSON

**362. Physicochemical determination of vitamin D. II. Alumina-liquid chromatography.** Katsutoshi Miwa (Hokkaido Reg. Fisheries Res. Lab., Yoichi). *Vitamins, Japan*, 1956, 11, 202-205.—Vitamin A (I) and calciferol (II) can be separated from each other by passing a soln. in light petroleum through a large chromatographic column (1.5 cm  $\times$  6 cm) of alumina; by this method the oxidised II is also separated from II. The amount of II which can be separated from 1000 i.u. of I within the range of low error (7%) by this method should not exceed 6000 i.u. and, in the presence of 1500 i.u. of I, poor results should be expected.

**III. Application of acid clay as adsorbent in chromatography.** Katsutoshi Miwa. *Ibid.*, 1956, 11, 552-555.—The chromatographic column (0.7 cm  $\times$  6 cm) packed with an acid clay, previously dried at 105° to 110°, is first washed with 15 ml of 7% ethanol-hexane and then with 10 ml of 10% diethyl ether-hexane, and can then be used for separating II from I. The recovery of II is 93 to 94%. For good results, the amount of I in the sample should be <800 i.u. A small amount of decomposition products of I contaminates the II fraction, so that samples containing <400 i.u. of II should not be used. Cholesterol gave the same values as II in this method so, if it is present, the sample should be pre-treated in order to remove it.

**IV. Selection of acid clay and developer.** Katsutoshi Miwa. *Ibid.*, 1956, 11, 556-558.—Four out of eight kinds of commercial acid clay gave good results. Good recoveries of II were obtained with *n*-hexane and 10% diethyl ether-hexane developer, and  $\text{CCl}_4$  or benzene as the developing solvent for II was found to be inferior to *n*-hexane. It is preferable to use *n*-hexane alone as developer for samples containing large amounts of I (7000 to 8000 i.u.).

CHEM. ABSTR.

**363. Spot test for vitamin B<sub>6</sub> [pyridoxine].** F. Feigl and E. Jungreis (Lab. da Produção Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Clin. Chim. Acta*, 1958, 3 (4), 399-400 (in English).—A drop of soln. or small fragment of solid in a micro test-tube is treated with 1 or 2 drops of cold satd. aq. soln. of molybdophosphoric acid. After brief warming, the soln. is centrifuged and the blue soln. discarded. The ppt. is suspended in 1 or 2 drops of  $\text{H}_2\text{O}$ , centrifuged, and the liquid is discarded. The ppt. is suspended in 2 drops of  $\text{H}_2\text{O}$ , 1 drop is placed on a piece of reagent paper (filter-paper soaked in a satd. soln. of 2:6-dichloro-*p*-benzoquinone-4-chlorimine and dried in air) and held over conc. aq.  $\text{NH}_3$  soln. The yellow ppt. disappears

and a blue stain appears if  $>0.5 \mu\text{g}$  of pyridoxine is present. Separation with molybdophosphoric acid is suggested as a possible method of isolation of the vitamin from multivitamin prep. before colorimetric determination.

H. F. W. KIRKPATRICK

See also Abstracts—49, Determination of Mg in food products. 208, Polarographic analysis of carbohydrates. 209, Separation and analysis of carbohydrates. 210, Chromatographic analysis of sugars.

### Sanitation

*Analysis of air, water, sewage, industrial wastes, industrial poisons.*

**364. Gas-liquid chromatographic analysis applied to air pollution. Sampling.** P. W. West, Buddhadev Sen and N. A. Gibson (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1958, 30 (8), 1390-1397.—A general method for the detection, determination and isolation of individual organic compounds in the atmosphere is described. Air samples are passed over a bed of cold, activated charcoal before chromatography. The method operates at 80% efficiency with a detection range between 1 and 50 p.p.m. when 20-litre samples are taken.

K. A. PROCTOR

**365. Rapid method for the determination of oxides of nitrogen in air.** L. A. Mokhov and V. S. Khal-turin. *Lab. Delo*, 1958, 4 (2), 26-27.—An indicator for the determination of oxides of nitrogen in air is prepared by adding the following reagents successively to silica gel (0.5 g)—0.2 ml of a saturated ethanolic soln. of benzidine hydrochloride, 0.1 ml of a 5% ethanolic soln. of 2-naphthol and 0.1 ml of a 0.1% ethanolic soln. of  $\text{NiCl}_2$ ; the silica gel is allowed to dry between the additions. The indicator is packed into a glass tube to form a 2-mm layer between two 3-mm layers of calcined quartz sand. To test for oxides of nitrogen, 100 ml of air is drawn through the tube in 30 sec. and after 1 to 2 min. the colour produced is compared with a series of standards prepared with samples of air containing 0.0005 to 0.1 mg of oxides of nitrogen per litre. The precision is  $\pm 3.5\%$ .

E. HAYES

**366. Determination of mercury in atmosphere.** U.K.A.E.A., Industrial Group (Chem. Services Dept., U.K.A.E.A., Capenhurst, England). U.K.A.E.A. Report IGO-AM/CA-173, 1958, 7 pp.—The method described by Buckell (*Brit. J. Ind. Med.*, 1951, 8, 181) is applied to the determination of Hg in the atmosphere in the presence of oil spray from vacuum pumps. *Procedure*—Draw the sample atmosphere through a series of three absorption towers packed with glass beads and containing acid permanganate soln. (satd.  $\text{KMnO}_4$  soln. -  $M \text{H}_2\text{SO}_4$ ) (4:1, by vol.). Pass at least 100 litres at a rate of 80 to 100 litres per hr. Combine the soln. from the three towers, and use  $\text{H}_2\text{O}_2$  (5 ml, of  $\approx 1$  vol. concn.) to wash out each tower; dilute the soln. and washings to 100 ml. To a 25-ml aliquot add hydroxylamine sulphate soln. (2 ml of 35%, w/v) and titrate with standardised dithionite soln. (0.0005%, w/v) by the extractive titration procedure. The method shows a negative bias of 3 to 5% on seven tests of atmospheres containing Hg in the range 30 to 200  $\mu\text{g}$  per cu. metre.

W. T. CARTER

367. **Determination of benzanthrone in air.** I. B. Kogan (Ukraine Inst. of Work Hygiene and Occupational Diseases). *Zavod. Lab.*, 1958, **24** (3), 291-293. —Three methods of determining benzanthrone or bromobenzanthrone are described—colorimetrically in conc.  $\text{H}_2\text{SO}_4$ , polarographically in 80% methanol with 0.1 N  $\text{H}_2\text{SO}_4$  as base electrolyte ( $E_1 = -0.9$  V), and by fluorescence in conc.  $\text{H}_2\text{SO}_4$ .

G. S. SMITH

368. **Determination of the chemical oxygen demand (C.O.D.) in waters and sewage with potassium dichromate.** P. L. Lapucci (Ist. di Igiene, Univ., Pisa, Italy). *Nuovi Ann. Igiene e Microbiol.*, 1958, **9** (2), 139-150. —A study is made of the method of Moore *et al.* (*Anal. Chem.*, 1949, **21**, 953). Although the oxidative power of  $\text{K}_2\text{Cr}_2\text{O}_7$  is less than that of  $\text{KMnO}_4$ , the  $\text{K}_2\text{Cr}_2\text{O}_7$  is easier to use, and gives consistent and reproducible results. In general, a direct relation between C.O.D. and B.O.D. does not exist. Nevertheless, a relation close to unity exists between these two factors for filtered sewage liquors, thus providing a rapid evaluation of B.O.D. from a knowledge of C.O.D. as determined by the above-mentioned method, but with 30%  $\text{H}_2\text{SO}_4$  instead of conc.  $\text{H}_2\text{SO}_4$ .

J. H. WATON

369. **Improvements relating to the measurement of oxygen dissolved in liquids [particularly boiler feed water].** Tinsley (Industrial Instruments) Ltd. [Inventors: B. Lamb and A. Rich]. Brit. Pat. 797,524; date appl. 19.1.55. —Small quantities of O present in industrial liquors are determined by means of polarographic analyses in which the liquid is caused to flow continuously past a pair of stationary electrodes. The cathode is of mercury-plated platinum, and the anode is a mercury pool.

J. M. JACOBS

370. **Determination of ammonia in water.** L. Krieger (Châtillon-en-Bazois, Nièvre, France). *Ann. Pharm. Franç.*, 1957, **15** (12), 731-732. —The water or standard is placed in the larger vessel of a Fleury "micro-Schloesing" apparatus and 1 ml of 0.01 N  $\text{H}_2\text{SO}_4$  is placed in the smaller vessel, which is supported inside it by a glass tripod. The apparatus is closed and heated at 37° for 30 min. After 1 ml of alkali soln. has been added to the water, the apparatus is closed and heated again at 37° for 24 hr. The contents of the small vessel are then treated with Nessler reagent and the absorption is measured with an electrophotometer (Meunier, filter 43, diaphragm 10).

E. J. H. BIRCH

371. **Nephelometric method for the determination of sulphate in water.** P. B. B. Vosloo and D. Sampson (Water Res. Div., Nat. Chem. Res. Lab., S. Africa). *S. Afr. Ind. Chem.*, 1958, **12** (3), 48-50. —The use of a photo-electric nephelometer, which measures the scattered light by means of several photocells surrounding the sample tube and its base, has been investigated, and the effects of pptn. vol., time interval between pptn. and measurement,  $\text{BaCl}_2$  crystal size and rate of dissolution, and temp. during pptn. have been studied. The following procedure was adopted for preparing samples and a standard graph. An aliquot is made up to 200 ml with distilled water in a 250-ml flask, and 5 ml of 5% HCl and 5 ml of 20% glycerol in ethanol are added. After mixing, a standard scoopful of  $\text{BaCl}_2$  is added, and, after shaking, the suspension is made up to 250 ml. Under standard conditions, the curve obtained by plotting nephelometer readings

against known concn. of sulphate is reproducible, but not linear.

A. M. SPRAAT

372. **Simplified fluoride distillation method.** E. Bellack (U.S. Public Health Service, Bethesda, Md., U.S.A.). *J. Amer. Wat. Wks. Ass.*, 1958, **50** (4), 530-535. —A fixed volume of water sample is distilled from a particular sulphuric acid mixture so that the same volume of distillate, with full recovery of fluoride, is obtained. Only standard items of equipment are required. Place 400 ml of distilled  $\text{H}_2\text{O}$ , 200 ml of conc.  $\text{H}_2\text{SO}_4$  and 2 to 3 dozen glass beads in a distilling flask. Swirl and connect up the distillation apparatus. Heat slowly and then rapidly till the flask contents are at 180°, exactly. The acid to water ratio has now been adjusted. Allow the contents to cool to 120°, add exactly 300 ml of water sample and distil as before until exactly 300 ml of distillate has been recovered. Periodic checking of the temp. at the end of a distillation will serve as a check on accuracy. The acid does not need replacing until the accumulation of ions causes carry-over of interferences. When the water sample contains high chloride content, add 5 mg of  $\text{Ag}_2\text{SO}_4$  per mg of chloride to the distilling flask. The method is simple, rapid and accurate.

G. HELMS

373. **Determination of fluorides in water.** J. Mayer and E. Hlucháň (Inst. Hyg., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (3), 143-154. —Three direct methods for the determination of fluorides (aluminon method, Chrome azurol S method and titration method) have been examined and the interference of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  studied. The titration method with the use of thorium nitrate as volumetric reagent and alizarin red S as indicator was found to be the most satisfactory. Sulphates can be separated as  $\text{BaSO}_4$ . *Procedure*—To 50 ml of the sample add 2 N NaCl (10 ml) and 3 drops of a satd. soln. of 2:4-dinitrophenol and titrate with 0.1 N HCl till colourless. Add 0.1 N HCl (1-5 ml), heat the soln. and precipitate  $\text{SO}_4^{2-}$  with  $\text{BaCl}_2$  soln.; boil and filter. Cool the filtrate, add alizarin red S as indicator and titrate with thorium nitrate soln.

J. ZÝKA

374. **Polarographic determination of iodine and bromine in mineral waters with the use of a solid anode.** N. N. Atamanenko and E. M. Skobets. *Ukr. Khim. Zhur.*, 1957, **23** (6), 771-776; *Ref. Zhur., Khim.*, 1958, Abstr. No. 46,421. —The method is based on the fact that in the oxidation of  $\text{Br}^-$  and  $\text{I}^-$  in soln. on the stationary or rotating platinum electrode, there are observed well-differentiated polarographic waves with sharp peaks, the heights of which are proportional to the concn. of  $\text{Br}^-$  and  $\text{I}^-$ . Evaporate 0.5 to 1 litre of the mineral water to be analysed to dryness on the water bath, dissolve the dry residue in 10 or 20 ml of water, add to 5 ml of the resulting soln. 15 ml of N HCl as basal soln. and polarograph. Then add a standard soln. of  $\text{Br}^-$  or  $\text{I}^-$  and once more polarograph. Calculation of the quantities of  $\text{Br}^-$  and  $\text{I}^-$  is carried out by the method of additions. It is established that by this method 0.1 mg of  $\text{I}^-$  (as I) can be readily detected.

C. D. KOPKIN

375. **Potentiometric determination of trichloroethylene in industrial waters.** Z. Deyl and M. Effenberger (Inst. Chem. Technol. of Water, High School of Chem. Technol., Prague). *Voda*, 1958, **37** (3), 90-92. —The potentiometric method with

the use of  $\text{AgNO}_3$  soln. enables trichloroethylene to be determined in the presence of chlorides without previous distillation. *Procedure*—To 100 ml of the sample add  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (1 g) and  $\text{HNO}_3$  (5%) (5 ml) and heat to boiling-point under reflux, the  $\text{HCl}$  liberated being absorbed in a wash-bottle containing water (20 ml). Cool and transfer the contents of the wash-bottle to the reaction vessel and titrate with 0.01 N  $\text{AgNO}_3$  with potentiometric control. In the presence of chlorides a blank must be carried out [without the decomposition with  $\text{HNO}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ]. J. ŽYKA

**376. Determination of petroleum products in sewage water by a pycnometric method.** Ya. I. Nel'kenbaum (Ishimbayev Petroleum Refining Works). *Zavod. Lab.*, 1958, **24** (3), 289-291.—The method is based on a determination of the reduction in sp. gr. of  $\text{CCl}_4$  after it has been used for the extraction of petroleum products. This requires a knowledge of the sp. gr. of the material to be extracted. When this is unknown, two separate extractions with different solvents,  $\text{CCl}_4$  and a mixture of  $\text{CCl}_4$  and benzene (sp. gr. 1.3 to 1.4), and corresponding measurements can be made.

G. S. SMITH

**377. The analysis of pyrethrins.** R. F. Phipers (Cooper Tech. Bureau, Berkhamsted, England). *Pyrethrum Post*, 1958, **4** (3), 3-7.—Recent publications of titrimetric, colorimetric, chromatographic and polarographic methods are reviewed.

E. G. BRICKELL

See also Abstracts—38. Determination of Cu in sea water. 117. Determination of P in water and effluents. 119. Determination of  $\text{PO}_4^{3-}$  in boiler water. 240. Determination of polycyclic hydrocarbons in smoke. 422. Gas-detecting apparatus. 425. Determination of dissolved O.

#### Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

**378. Determination of very small amounts of zinc in soils, plant and animal materials and fertilisers.** K. Scharrer and H. Munk (Agrik.-chem. Inst. Univ. Giessen, Germany). *Z. PflErnähr. Düng.*, 1956, **74**, 24-42.—After removal of organic matter from the sample by wet- or dry-ashing (details are given for soils, plant material and fertilisers) and dissolution in  $\text{HCl}$ , an aliquot containing 1 to 80  $\mu\text{g}$  of Zn is taken for analysis. Sufficient acetate buffer (pH 6.0) (Na acetate, 300 g, glacial acetic acid, 10 ml, citric acid, 30 g, water to 1 litre, heavy metals being extracted by dithizone) is added to give a pH of 5.0, the soln. then being diluted to 50 ml. Dithizone (0.05% in toluene) (30 ml) is added and the mixture is shaken for 2 min. in a separating funnel. The separated toluene layer is washed with 1%  $\text{Na}_2\text{S}$  soln. (20 ml) and then 3 times with water. According to the amount of Zn present, as indicated by the pink colour, 20, 10 or 6 ml of 0.08 N  $\text{HCl}$  is added. After shaking (2 min.) and when the aq. phase has become clear, 5 ml of the aq. phase is removed and to it are added 5 ml of a phosphate buffer (pH 6.7), 4 ml of indo-oxine soln. (200 mg in 1 litre of ethanol) and, after 30 min., water to make a total vol. of 50 ml. The colour is determined photometrically by comparison with standard zinc soln.

A. G. POLLARD

**379. Determination of small amounts of molybdenum in agricultural analysis.** K. Scharrer and W. Eberhardt (Agrik.-chem. Inst. Univ. Giessen, Germany). *Z. PflErnähr. Düng.*, 1956, **73**, 115-127.—Appropriate extracts of soil, plant or other org. material are ashed by dry (500° for 3 hr.) or wet ( $\text{HNO}_3$ - $\text{HClO}_4$ ) methods;  $\text{HCl}$  extracts are treated only by the wet method. To the residue in 1 to 2%  $\text{H}_2\text{SO}_4$  is added 1 ml of 2% benzoin  $\alpha$ -oxime in alcohol and after shaking for 30 min. the Mo complex is extracted ( $\times 2$ ) with  $\text{CHCl}_3$ . After removal of solvent, the residue is heated with  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  (each 0.5 ml), 3 to 5 drops of freshly distilled  $\text{HNO}_3$  and 1 ml of bismuth nitrate soln. (100 mg of Bi per ml) until dry. The white residue is dissolved in 20 ml of  $\text{HCl}$  and 7.5 ml of Na citrate soln. (20 g of citric acid, 20 ml of 10 N  $\text{NaOH}$  and 280 ml of  $\text{H}_2\text{O}$ ) is added, followed by 2.5 ml of dithiol reagent [1 g of dithiol in 500 ml of 0.25 N  $\text{NaOH}$ , to which is added 2.5 ml of 80% thioglycolic acid; the filtered soln. is stored in small (25 to 50-ml) flasks in ice]. After 30 to 45 min. the molybdenum complex is extracted with butyl acetate (16.5 ml, for 15 sec.). The extract is filtered and diluted to 25 ml. The colour density is determined with ELKO filter 66.1; 0.25  $\mu\text{g}$  of Mo may be determined with an error of  $\pm 5\%$  and 0.1  $\mu\text{g}$  with an error of  $\pm 10\%$ . The test soln. should contain 0.006 to 0.015  $\mu\text{g}$  of Mo per ml.

A. G. POLLARD

**380. Determination of traces of manganese with leucomalachite green.** S. H. Yuen (I.C.I. Ltd., Jealott's Hill Res. Sta., Bracknell, Berks., England). *Analyst*, 1958, **83**, 350-356.—The method described has been applied to plant material and to ammonium acetate extracts of soil, and its possible application in water analysis is suggested. The plant material (0.1 g) is ignited at 550°, the residue is dissolved in dil.  $\text{HCl}$  and the soln. is evaporated to dryness. The soln. of the gently ignited residue in  $\approx 7$  N  $\text{HCl}$  is extracted with diisopropyl ether, the extract is rejected, the aq. layer is evaporated to dryness, and the residue is dissolved in acidulated water, boiled and filtered. An aliquot of the extract ( $\approx 1 \mu\text{g}$  of Mn) is diluted, and mixed with a Na acetate-acetic acid buffer soln. and 5 ml of 0.2%  $\text{KIO}_4$  soln. The liquid, thermostatically controlled at 25°, is treated with 1 ml of 0.1% leucomalachite green soln. (prep. described) and after 1 hr. the extinction is measured against water at 620  $\text{m}\mu$ . The result corrected for a blank determination is referred to a calibration graph. The sensitivity of the method can be increased by extracting the colour with a small vol. of  $\text{CHCl}_3$ . Amounts of 36 ions that may be present without causing interference are quoted. The precision of the method is  $\approx \pm 5\%$ .

A. O. JONES

**381. Determination of carbonates in soils.** C. J. Schollenberger and C. W. Whitaker (Ohio Agric. Exp. Sta.). *Soil Sci.*, 1958, **85**, 10-13.—Carbonates are decomposed by N  $\text{HCl}$  containing  $\text{SnCl}_4$  (26 g per litre) and the  $\text{CO}_2$  is trapped in  $\text{Ba}(\text{OH})_2$ . The improved apparatus described provides a closed system with re-circulation of the gas to ensure complete absorption by  $\text{Ba}(\text{OH})_2$ ; the whole apparatus is mounted on an eccentric rocking device. The temp. of the reaction vessel is controlled (50° for soils containing dolomite) and the titration is carried out without exposure to the air. Samples of up to 100 g may be used, but should not contain  $> 0.25$  g of  $\text{CaCO}_3$ .

A. G. POLLARD



382. Flame-photometric determination of barium in Mehlich's method for measuring the exchange capacity of soils. D. Schroeder (Inst. Bodenkunde, Tech. Hochschule, Hannover). *Z. Pflernähr. Düng.*, 1956, **73**, 86-87.—Determinations of Ba displaced from soil by leaching with 0.2 N  $MgCl_2$  (Mehlich, *J. Ass. Off. Agric. Chem.*, 1953, **36**, 445) are made by the flame photometer with the hydrogen flame at 515 m $\mu$  or 873 m $\mu$ . Neither Mg nor the small amounts of Ca likely to be present in the  $MgCl_2$  leachates interfere. The errors with soln. containing 2 and 10 milli-equiv. of Ba were, respectively, 1.7 and 1.1% (873 m $\mu$ ) and 4.7 and 1.2% (515 m $\mu$ ). A. G. POLLARD

383. Semi-quantitative determination of vanadium in soils by paper chromatography. H. Agrinier. *Compt. Rend.*, 1958, **246**, 2761-2763.—A separation of V is obtained by the use of a solvent composed of ammonia and oxygenated water, and development with 8-hydroxyquinoline. The limit of sensitivity is  $\approx 0.005 \mu g$  of V. For the determination of V in uranium minerals, previous separation of U by isobutyl methyl ketone is recommended. R. A. HOWIE

384. Spectrochemical determination of trace elements [in soils]. K. Scharrer and G. K. Judel (Agrik.-chem. Inst. Univ. Giessen, Germany). *Z. Pflernähr. Düng.*, 1956, **73**, 107-115.—The technique and standardisation of the spectrochemical procedure (with Fe as reference element) for determining Co, Cu, Mn, Mo, Ni, Pb, Sn and V in soils are examined. The soil (40 g), preferably after overnight ignition in a muffle-furnace at 450°, is extracted with 10% HCl. Iron is determined (2:2'-dipyridyl) in the extract. To an aliquot, containing exactly 40 mg of Fe, is added aq.  $NH_3$  to bring the pH to 4.8. Sulphosalicylic acid is added to form complexes of alkali and alkaline-earth metals, Al and Ti (Stetter and Exler, *Naturwissenschaften*, 1955, **42**, 45), followed by Na tetramethylenedithiocarbamate to precipitate heavy metals, and the ppt. is extracted with  $CHCl_3$ . The extract is evaporated to dryness and the residue ignited at 450° overnight. The ash is mixed with NaCl and pure carbon (1:1:3) for the determination. Data for 30 soils and a comparison with photometric methods are recorded. The mean errors as a percentage of the amount present were Co  $\pm 1.8$ , Cu  $\pm 3.2$ , Mn  $\pm 7.1$ , Mo  $\pm 5.4$ , Ni  $\pm 1.6$  and Zn  $\pm 5.0$ . A. G. POLLARD

385. Fineness of fertiliser samples. H. S. Howes (Waterfall & O'Brien, 4 Queen Sq., Bristol, England). *Analyst*, 1958, **83**, 379.—With some concentrated fertilisers, such as those in which the ratio of N to  $P_2O_5$  to  $K_2O$  is 10:10:16, duplicate 2-g samples drawn after passing the material through a 22-mesh sieve failed to give the same analyses. This was found to be due to the use in manufacture of a new crystal form of  $(NH_4)_2SO_4$ , namely short thick prisms that escape fracture and tend to separate in the sampling. Grinding of the sample to pass a 30-mesh sieve leads to uniform distribution, and analyses of duplicate portions then agree closely. The 22-mesh sieve is somewhat finer than the sieve with apertures 1 mm square recommended in the Fertilisers and Feeding Stuffs Regulations 1955. A. O. JONES

386. Analysis of manures; field evaluation of contents of nitrogen and potash by densitometry. E. Jouis and E. Hangard. *Chim. et Ind.*, 1958, **79**

(4), 451-454.—Analyses of farm manures (*Ann. Agron., Paris*, 1955, **2**, 301) are reviewed. Liquids from dung-heaps may contain 0.2 to 1 kg of N and 1 to 5 kg of  $K_2O$  per cu. metre, whilst urinous liquids may contain 5 to 10 kg of N and 10 to 15 kg of  $K_2O$  per cu. metre. These figures can be quite different from those for normal stable manure. The contents of N and  $K_2O$  in a liquid manure on site can be rapidly evaluated by referring the reading obtained with an apple-must densimeter to the tables provided, namely  $d$  vs.  $(N + K_2O)$  in g per litre, and  $d$  vs.  $N/(N + K_2O)\%$ . The values for N and  $K_2O$  are each within  $\approx \pm 0.3\%$  of those obtained by chemical analysis. W. J. BAKER

387. Analysis of superphosphates. III. Volumetric determination of assimilable phosphorus as lead phosphate in the presence of dithizone as indicator. M. Vancea and M. Volușniuc (Inst. of Chem., Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1957, **8** (3-4), 261-264.—Procedure—Between 20 and 30 ml of an aq. acetic acid (3%) extract of the superphosphate is treated with 5 ml of acetic acid-acetate buffer, and 3 ml of a satd. soln. of  $Ba(NO_3)_2$  is added dropwise with continuous stirring in the cold. A freshly prepared soln. (1 ml) of dithizone (0.01 g in 100 ml of  $CHCl_3$ ) is added to the supernatant liquid, with gentle shaking, followed by 0.05 N Pb acetate until the colour changes from green to violet. The titre of the Pb acetate soln. is determined under identical conditions. The method can be used for control of the manufacture of fatty materials containing phosphates.

IV. Direct volumetric titration of assimilable phosphorus as bismuth phosphate with dithizone as indicator. M. Vancea and M. Volușniuc. *Ibid.*, 1957, **8** (3-4), 265-268.—Procedure—To 10 ml of a soln. of superphosphate are added 2 to 5 ml of acetic acid-acetate buffer and 1 ml of a soln. of dithizone (0.01 g in 100 ml of  $CHCl_3$ ). The soln. is titrated slowly with standard  $Bi(NO_3)_3$  soln. ( $> 5$  g of Bi per litre) with continuous stirring until the colour changes from green through orange and brown to grey. H. SHER

388. Determination of phosphate ions in manures by precipitation as bismuth phosphate and titration with EDTA (disodium salt). E. Jouis (Sta. Agron., Rouen, France). *Sciencaf Studoj, Internac. Sci. Asoc. Esperantista*, 1958, 181-185.—The sample is ashed, the residue is dissolved in  $HNO_3$  and the soln. diluted with  $H_2O$  to a concn. equiv. to about 1 g of dry manure in 50 ml. Excess of  $HNO_3$  is neutralised (to thymol blue) with triethanolamine and the colour brought to pink by addition of dil.  $HNO_3$ . The phosphate is pptd. hot by addition to  $Bi(NO_3)_3$  soln. (adjusted to a pH of 1.5 to 1.9 and containing mannose to prevent pptn. of other bismuth compounds) and, after 1 hr. at 80°, the soln. is diluted to 100 ml with  $H_2O$  and filtered. In an aliquot portion, adjusted to a pH of 1.5 to 2.0, the excess of Bi is titrated with EDTA (disodium salt) soln. D. R. DUNCAN

389. Determination of spray deposits of chlorobenzilate (ethyl pp'-dichlorobenzilate). E. J. Skerrett and E. A. Baker (Long Ashton Res. Sta., Bristol, England). *Ann. Rep. Agric. Hort. Res. Sta., Bristol*, 1956 (1957), 130-134.—A modification of the Harris method (*Anal. Abstr.*, 1956, **3**, 1541) is described. Leaf disc samples are extracted with  $CCl_4$  ( $\times 3$ ) in a Soxhlet apparatus, 2 ml of a 0.5% soln. of stearic acid in light petroleum (boiling-

range 40° to 60° being added to the extraction flask immediately before the fourth siphoning. The solvent is removed (56° and 21 cm Hg pressure) and the residue is nitrated with 5 ml of a mixture of equal vol. of  $H_2SO_4$  and  $HNO_3$  (sp. gr. 1.5) in a boiling-water bath (air condenser) for 1 hr. After cooling the product in ice water, 50 ml of satd.  $Na_2SO_4$  soln. (treated with  $SO_2$  to depress mould growth) is added to the flask and the mixture is transferred to a 125-ml separating funnel with 70 ml of ether and 25 ml of  $Na_2SO_4$  soln. After shaking, the aq. layer is removed and the ether soln. is washed with 25 ml and 10 ml of 5% KOH soln. and 15 ml of satd.  $Na_2SO_4$  soln. The ether layer is percolated through a 15-ml layer of anhyd.  $Na_2SO_4$  and the solvent is evaporated on a water bath at 56°. The residue is dissolved in 0.5 ml of 2-ethoxyethanol and treated with 10 ml of 5% KOH soln. in methanol. The absorption is measured (538  $m\mu$ ) after 30 min. A. G. POLLARD

**390. Determination of chlorinated hydrocarbon pesticide residues in plant material.** G. A. Sergeant (Dept. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1958, **83**, 335-339.—After extraction and partial purification, the residues are analysed for total org. Cl by a modified Stepanow procedure, followed, after removal of org. matter and excess of  $Na^+$ , by determination of  $Cl^-$  by mercuric oxycyanide. Recoveries with various pesticides added to vegetable material are satisfactory. The method is not successful with Kelthane, which is strongly adsorbed on the alumina. A. O. JONES

**391. Determination of DDT in plant materials and soil.** J. T. Martin and R. F. Batt (Long Ashton Res. Sta., Bristol, England). *Analyst*, 1958, **83**, 340-344.—Two procedures based on nitration and colour formation with ethanolic KOH are described. In the first, DDT is determined in the range 0 to 350  $\mu g$  and, in the second, in the range 0 to 30  $\mu g$ . Methods of overcoming interference by wax and pigments are described. The recovery of added amounts is satisfactory. A. O. JONES

**392. Spectrophotometric determination of parathion and p-nitrophenol.** E. Hjelt and A.-L. Mukula (Inst. of Forensic Med., Univ. of Helsinki, Finland). *Analyst*, 1958, **83**, 283-290.—Three equal aliquots of a soln. of parathion in an organic solvent are evaporated under reduced pressure at 50°. In a specially designed flask one residue is hydrolysed by heating with KOH soln. and extracted with a benzene-acetone mixture. An aliquot of the extract is mixed with acetone and its extinction is measured at 420  $m\mu$  (soln. A). The second residue is heated under reflux with benzene and KOH soln., shaken after addition of acetone and its extinction is measured at 420  $m\mu$  (soln. B). The third residue is dissolved in 94% ethanol and its extinction is measured at 280  $m\mu$  against the solvent (soln. C). The extinctions of A and B are measured against the benzene-acetone mixture which has been shaken with aq. KOH. From the measured extinctions and the known mol. extinctions of p-nitrophenol in soln. A and B and of parathion in soln. C the amounts of parathion and p-nitrophenol in the sample and the amount of p-nitrophenol formed by hydrolysis can be calculated. p-Nitrophenol is detected in the hydrolysed and unhydrolysed material by ascending paper chromatography with isobutyl and isoamyl alcohols

(1 + 1) saturated with  $NH_3$  as solvent, the spots being detected by spraying with aq.  $NH_3$  or alkali. A. O. JONES

See also Abstract—377, Analysis of pyrethrins.

## 5.—GENERAL TECHNIQUE AND APPARATUS

### General

**393. Simple recording balance.** P. C. Scholten, W. M. Smit and M. D. Wijnen (Lab. of Anal. Chem., State Univ., Utrecht). *Rec. Trav. Chim. Pays-Bas*, 1958, **77** (4), 305-315 (in English).—The balance described comprises a simple analytical balance, an electronic part, and a recorder, which is mechanically indifferent and has a movable electrical zero-point. The compensating force is free from any gravitational component and equilibrium is attained without restoration to an initial position. The sensitivity may be changed from 25 to 200 mg (full-scale deflection) and the accuracy is 0.3% of full-scale deflection. Its use as a thermobalance is described. M. DAVIS

**394. Improvements in or relating to burettes [operating by means of diminished atmospheric pressure].** W. Albién. Brit. Pat. 799,255; date appl. 16.10.56.—The burette comprises a measuring tube, a liquid-supply duct extending from the measuring tube to a point always below the liquid-supply level, and a suction duct extending from the top of the measuring tube to a rubber bulb, the arrangement being such that the required quantity of titration liquid can be delivered from the burette by a single compression of the rubber bulb by the operator's hand. J. M. JACOBS

**395. Countercurrent distribution: quantitative analysis of results, especially where separation is incomplete.** A. A. Levi (Res. Dept., I.C.I. Pharm. Division, Hexagon House, Blackley, Manchester, England). *Biochem. J.*, 1958, **69** (4), 516-523.—A "least squares" method is described for the calculation of the amount of a material in a zone containing a single substance after countercurrent extraction. The method can be extended to give a "best estimate" of the partition ratio of a substance, and to the calculation of the composition of zones formed by mixtures. The method can be used for the determination of each of a pair of substances difficult to separate or to determine in the presence of each other. It is not limited to two components, and can also be used for substances whose partition ratios are similar. J. N. ASHLEY

**396. A simple melt-viscometer for very high viscosities.** P. A. Small (I.C.I., Welwyn Gdn. City, Herts., England). *J. Polym. Sci.*, 1958, **28** (116), 223-224.—The viscometer described was designed for the characterisation of hydrocarbon polymers available in small quantities (0.1 g). Viscosities between  $10^4$  and  $10^6$  poises can be measured. B. J. WALBY

**397. Rotatory viscometer with a stroboscopic disc.** K. Rehaček. *Chem. Průmysl*, 1958, **8** (7), 365-366.—The viscometer (illustrated) is suitable for measuring viscosity of thick liquids. Measurements can be made in vessels of different diameters if a suitable factor for the influence of the walls is applied. The precision is  $\approx \pm 5\%$ . N. E.

398. Enzymic studies in small amounts of human tissue with the help of micro-analytical methods. I. Micro-spirometer for the measurement of oxygen consumption of human liver samples removed by biopsy puncture. J. Frei and H. Ryser (Lab. de Biochim., Clin. Med. Univ., Lausanne, Switzerland). *Clin. Chim. Acta*, 1958, **3** (3), 288-297 (in English).—An all-glass micro-manometer is described that measures the oxygen uptake by milligram amounts of fresh tissue with the same accuracy as does Warburg's manometer.

II. Oxidative phosphorylation in human liver samples removed by biopsy puncture. J. Frei and H. Ryser. *Ibid.*, 1958, **3** (3), 294-297 (in English).—A micro-technique is described, by which about 3 mg of fresh tissue is used.

H. F. W. KIRKPATRICK

399. A simplified semi-automatic [pharmacological] bio-assay apparatus. C. E. Rapela and E. A. Conrad (Wake Forest Coll., Winston-Salem, N.C., U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (3), 469-472.—The construction of a simple inexpensive semi-automatic apparatus for controlling the addition of soln. to an isolated organ bath and the use of the apparatus in catecholamine determinations with the isolated rat uterus are described. Possible applications of the equipment include the bio-assay of adrenaline, noradrenaline, antihistamines, curare-like drugs and spasmolytic agents.

W. H. C. SHAW

#### Chromatography, ion exchange, electrophoresis

400. An apparatus for chromatography at reduced temperatures. W. Hüchel and W. Hornung (Pharm.-Chem. Inst., Univ., Tübingen, Germany). *Chem. Ber.*, 1957, **90**, 2023-2024.—An apparatus is described for use at  $-78^{\circ}$ .

C. A. SLATER

401. Chromatographic analysing and recording apparatus. Technicon International, Ltd. Brit. Pat. 798,920; date appl. 6.11.56 (date appl. U.S.A., 21.11.55).—The apparatus comprises a column into which an adsorbate is introduced. After addition of a suitable colour-developing reagent, successive portions of the eluate are transferred to a flow-cell colorimeter for colorimetric analyses. Provision is made in the colorimeter for automatically transmitting light of different predetermined wavelengths through the eluate for controlling a recorder to provide individual colorimetric recordings in respect of the eluate for each selected light transmission.

J. M. JACOBS

402. Simplified technique for the preparation of glass paper impregnated with silicic acid. J. W. Dieckert, W. B. Carney, R. L. Ory and N. J. Morris (Southern Utilization Res. and Development Div., U.S. Dept. of Agric., New Orleans, La.). *Anal. Chem.*, 1958, **30** (8), 1442.—Methods for removing organic impurities from glass paper to be used for paper chromatography and for impregnating the paper with silicic acid, to overcome the difficulties caused by weak paper, are described. Comparative results are given of tests with paper prepared by the new method and paper prepared by the technique of Dieckert and Reiser (*cf. Anal. Abstr.*, 1955, **2**, 1736; 1957, **4**, 4082).

F. L. SELFE

403. Quantitative evaluation of paper chromatograms from changes in impedance. M. Hejtmánek and J. Hejtmánková (Inst. Phys. Chem. and Anal. Chem., High-School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (3), 444-449.—The use of high-frequency measurements of impedance changes for the determination of the character of the dependence of the concn. of the compound to be determined on the distance travelled on paper chromatograms has been studied. The paper strip is moved between two electrodes connected in the circuit of a high-frequency oscillator. A new simple apparatus for automatic registration is described.

J. ZÝKA

404. Gas-liquid chromatography: effect of support size and proportion of liquid phase on column efficiency. J. D. Cheshire and R. P. W. Scott. *J. Inst. Petrol.*, 1958, **44**, 74-79.—Tests with hydrocarbons carried by N-H (1:3) in a column of graded insulating brick treated with Apiezon oil A showed that the efficiency ( $E$  theoretical plates) was higher for smaller gradings provided that the size range was narrow, e.g., 100 to 120 B.S. mesh. To avoid the adverse effects of liquid diffusion, the oil should be spread thinly through the column; with  $>5\%$  w/w of oil,  $E$  is almost linearly proportional to the length of the column. A column (length 25 ft., diam. 3.6 mm), with 60 to 100-mesh packing containing 5% of oil, through which the gas flowed at 37 ml per min., separated 11 hydrocarbons ( $C_6$  to  $C_8$ ), only  $p$ - and  $m$ -xylene showing a double peak. Values for  $E$  of 10,000 to 12,000 can be obtained.

A. R. PEARSON

405. Low-pressure electric discharge detectors. R. C. Pitkethly (The British Petroleum Co., Ltd., Sunbury-on-Thames, Middx, England). *Anal. Chem.*, 1958, **30** (8), 1309-1314.—The vapour-phase chromatographic detection device of Hartley and Pretorius (*Nature*, 1956, **178**, 1244) has been modified by the use of a homogeneous, non-sputtering cathode and a small anode-cathode spacing in order to ensure stability and sensitivity. Concn. of paraffin hydrocarbons of 1 in  $10^7$  can be detected, and the peak-height response to propane and the butanes is linear over the range  $10^{-11}$  to  $10^{-8}$  mole.

K. A. PROCTOR

406. Simple apparatus for washing paper strips for electrophoresis. E. B. L. M. Van Nispen Tot Pannerdea (St. Elisabeth's Gasthuis, Arnhem, The Netherlands). *Clin. Chim. Acta*, 1958, **3** (3), 300-301 (in English).—Dry strips are suspended in a special cylinder, stained, and then washed by circulation of the soln., either by an electric synchronous motor or by air from a cylinder.

H. F. W. KIRKPATRICK

407. A curve plotter for the Kern electrophoresis apparatus Model LK30. W. Lotmar (Kern & Co. Ltd., Aarau, Switzerland). *Clin. Chim. Acta*, 1958, **3** (3), 301-303.—An apparatus that gives rapid and semi-automatic plotting of the concn. curve is described.

H. F. W. KIRKPATRICK

408. Controls for electrophoresis in agar jelly. C. H. Wunderly (Med. Univ. Clinic, Zurich, Switzerland). *Clin. Chim. Acta*, 1958 **3** (3), 298-299 (in English).—A 35% colloidal sol of dextran (mol. wt. 150 to  $200 \times 10^4$ ) is employed as the base soln. of two dyes that are used to indicate that electrophoresis is proceeding normally. One is prepared

by colouring the dextran a deep blue with bromophenol blue and the other by colouring it brown with o-nitroaniline. The indicators are added as spots after diffusion of the sera into the gel. When electrophoretic migration has started, the brown indicator moves towards the cathode, propelled by electro-osmotic flow, and the blue towards the anode, some with the albumin front and some (excess) ahead of it. Both indicators show a constant but different mobility which can be checked at intervals by measurement with a ruler.

H. F. W. KIRKPATRICK

See also Abstracts—232. Apparatus for spectrochromatography. 315. High-frequency recording in chromatography.

### Optical

409. **Fluorescent sources for X-ray diffractometry.** W. Parrish, K. Lowitzsch and N. Spielberg (Philips Lab., Irvington-on-Hudson, New York, U.S.A.). *Acta Cryst.*, 1958, **11**, 400-405.—Two types of fluorescent source are described and the results are compared with those obtained when a standard diffractometer with conventional X-ray tube source is used. The brightness of these two sources was extremely low and for conditions of comparable resolution the intensities were about a few tenths of 1% of those obtained with the conventional source. The effects of instrumental factors on line width and the reason for the large decrease in intensity are discussed.

K. A. PROCTOR

410. **Three-prism spectroscope of very high light intensity.** E. Kleimon. *Chem. Tech., Berlin*, 1958, **10** (3), 157-159.—Details of construction are given for a spectroscope for the range 360 to 656 mμ, of high light intensity and very high linear dispersion.

J. L. PROSSER

411. **Evaluating procedures employed in the method of successive addition in spectral analysis.** Z. Nagy (Inst. of Med. Chem., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (1-2), 107-112 (in English).—The evaluation of the concn. of an unknown soln. by spectrographic measurements on this unknown without the isolation of the pure unknown compound is described. Two further aliquots of the unknown soln. are taken and to them known quantities of an internal standard are added. From the basic equation,  $I_a/I_s = k \times (c_a/c_s)^n$ , where  $I_a$  and  $I_s$  are the intensities and  $c_a$  and  $c_s$  are the concentrations and concn. of the unknown element and the internal standard element, respectively, the equation,

$$1 + a_2x = (1 + a_1x)^\beta,$$

has been derived, where  $a_1$  and  $a_2$  are the two known added concn.,  $x = 1/c$ ,  $c$  being  $c_a/c_s$ , and  $\beta$  is the quotient of the logarithms of the quotients of the corresponding intensity ratios.  $\beta$  may be determined from the measured differences in the corresponding photographic line blackenings. The resulting equation is solved for  $x$  graphically or by nomograms.

E. G. CUMMINS

412. **Spectrographic analysis of certain elements in an atmosphere of carbon dioxide.** S. K. Kalinin, V. L. Marzuvanov and É. E. Fain. *Vestn. Akad. Nauk KazSSR*, 1957, (12), 61-69; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,327.—The properties of

an arc discharge in an atmosphere of  $\text{CO}_2$  are studied. Carbon electrodes were inserted into a quartz tube, in which a stream of  $\text{CO}_2$  for a few seconds displaces the air. By using a mixture of  $\text{SiO}_2$ , KCl and carbon with arc discharge at 9 amp., it is shown that in an atmosphere of  $\text{CO}_2$  the temperature of the discharge increases and the size of the arc cloud decreases. The temperature of the discharge in  $\text{CO}_2$  is little influenced by the current strength. There is observed a very rapid burning of the electrodes in the arc discharge in  $\text{CO}_2$ , and elimination of the bands due to CN. This last creates favourable conditions for analysis by the use of lines which are normally covered by the molecular bands.

C. D. KOPKIN

413. **Double monochromation in ultra-violet micro-spectrophotometry.** H. A. Stahl (Dept. of Path. and Ontology, Univ. of Kansas Med. Centre, Kansas City, U.S.A.). *Science*, 1958, **127**, 1290-1291.—Conversion of a single monochromatic double-beam micro-spectrophotometer into a double monochromatic instrument is described.

H. F. W. KIRKPATRICK

414. **Scattered X-rays as internal standards in X-ray emission spectroscopy.** G. Andermann and J. W. Kemp (Appl. Res. Lab., Glendale 8, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1306-1309.—The use of radiation, scattered by the sample, as an internal standard corrects partially or wholly for instrumental variation and absorption effects.

K. A. PROCTOR

415. **X-ray-spectrographic study of chemical composition in micro-volumes of alloys.** I. B. Borovskii, N. P. Il'in, L. E. Loseva, I. D. Marchukova and A. N. Deev. *Izv. Akad. Nauk, SSSR, Ser. Fiz.*, 1957, **21** (10), 1415-1423; *Ref. Zhur., Khim.*, 1958, Abstr. No. 53,379.—A short description is given of apparatus RSASh-2, designed for the study of the micro-composition of complex samples. An electron gun is aligned with magnetic lenses on to the surface of the sample. The diameter of the focal spot is 2 or 3 μ. The electrons excite the atoms in a volume of  $\approx 10$  cu. μ. The X-radiation is studied by the normal methods of X-ray spectrographic analysis with a curved quartz single crystal (1010) and a Geiger-Müller counter. The mean sensitivity of the method (0.1%) enables  $10^{-12}$  g of an element to be determined. The sample may be continuously moved under the electron gun at a speed of 10 to 150 μ per min. The line intensity of the element being analysed is inscribed on the tape of a self-registering potentiometer. To investigate the possibilities of the instrument, the analysis of the homogeneity of an alloy, the composition of phases, welded and fused joints and diffusion layers was carried out. The authors conclude that the new method of analysis allows the highly accurate study of the topographical distribution of elements in alloys, and may find wide application in metal-behaviour and the physics of metals. (See also *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,300.)

C. D. KOPKIN

416. **Electron probe micro-analyser and its application to ferrous metallurgy.** R. Castaing, J. Philibert and C. Crussard (Univ. de Toulouse, France). *J. Metals, N.Y.*, 1957, **9** (4), 389-394.—A finely focused beam of electrons is projected on to the surface of a sample and the X-ray spectrum emitted from the irradiated portion is analysed for wavelength and intensity. This point-analysis



has been applied to the study of numerous metallurgical problems (selective oxidation during scaling, phase equilibria and identity, and studies of diffusion).  
G. SKIRROW

**417. Analysis of gases and vapours, based on the negative optical-acoustical effect.** M. L. Veingerov, A. A. Sivkov and E. V. Malykh. *Optika i Spektroskopiya*, 1957, 2 (6), 823-825; Ref. Zhur., Khim., 1958, Abstr. No. 21,125.—A method is described for the optical-acoustical analysis of gases, based on the modulation by a rotating perforated disc of the process of heat transfer by radiation from the gas to a condenser. Working on this principle the method detects  $\approx 0.5\%$  of  $\text{CO}_2$  in air. The described method may be applied to the analysis of gases by the use of long wave bands (up to  $50\ \mu$ ), and when there may be danger of explosion from ignition of the gases.  
C. D. KOPKIN

#### Thermal

**418. Vacuum-fusion apparatus for gas analysis.** P. D. Blake. *J. Iron St. Inst.*, 1958, 188 (3), 261-264.—The apparatus described is suitable for the determination of the total oxygen and fractional oxygen content of steel. It is a modification of the Speight and Cook apparatus (cf. *J. Iron St. Inst.*, 1954, 176, 252), the principal difference being the incorporation of a dual analytical system suitable for either low pressures and gas volumes  $> 2\ \text{ml}$ , or for medium pressures and gas volumes  $> 2\ \text{ml}$ . Results of determinations of O obtained with this apparatus and the NPL and alcoholic iodine methods of Garside *et al.* (cf. *J. Iron St. Inst.*, 1957, 185, 95) are compared. J. W. O. PYEMONT

**419. Differential thermal analysis apparatus.** D. F. Arseneau (Xavier Junior Coll., Sydney, Nova Scotia, Canada). *J. Chem. Educ.*, 1958, 35 (3), 130.—A modification of Borchardt's apparatus (cf. *J. Chem. Educ.*, 1956, 33, 103) is described and illustrated. A rod of the same material as the differential thermal analysis apparatus is fitted into the original sample holder, so that the upper drill hole becomes the sample holder and the lower drill hole prevents damage to the thermocouples. Analyses of liquids and fusible solids are described.  
O. M. WHITTON

**420. A new apparatus for differential thermal analysis.** V. Šiške and I. Proks (Inst. Inorg. Chem., High-School of Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, 12 (3), 185-189.—In the apparatus described, the sample as well as the standard are moved at a regulated speed into the heated furnace. This arrangement enables as little as 0.02 g of sample to be used. J. ŽYKA

**421. Design of a graphically recording vacuum micro-thermobarometer based on the MacBain balance.** P. Barret (Lab. de Chim. M.P.C., Fac. des Sci., Boulevard Gabriel, Dijon, France). *Bull. Soc. Chim. France*, 1958, (3), 376.—An arrangement is described in which an image of the pointer (a blackened quartz fibre) of a quartz-helix thermobarometer is projected on to a spot-following apparatus feeding a recorder. The difficulty that such an apparatus is usually arranged to work with a bright spot on a dark ground, whereas in this case there is a dark image on a bright ground, is overcome by an appropriately shaped diaphragm on the cadmium sulphide cell. The range and accuracy of the apparatus are discussed.  
E. J. H. BIRCH

#### Electrical

**422. Improvements relating to gas-detecting apparatus.** J. W. Zwicky and D. E. Chandler. Brit. Pat. 797,835; date appl. 4.4.55.—The device comprises a cell of insulating material, having a pair of electrodes located in its wall, and a de-ionisation column filled with ion-exchange resin. Water is circulated through the vessels until it reaches a state of max. de-ionisation with consequent max. electrical resistance (measured by a Wheatstone-bridge circuit containing a galvanometer). The gas or mixture of gases is drawn or forced into the cell and the drop in the electrical resistance is measured. The rate of fall depends on the rate of gas flow, the relative solubility of the gas or gases and their degree of ionic dissociation under the existing conditions of temp. and pressure. It is therefore possible to determine when a desired concn. of gas in solution has been reached. The device can be used, for example, to indicate when an excessive amount of  $\text{CO}_2$  is present in air or in flue gases.  
J. M. JACOBS

**423. Apparatus for measuring the impurity content of liquids.** W. Crockatt & Sons, Ltd., and W. C. Crockatt. Brit. Pat. 797,752; date appl. 31.3.54.—A temperature-compensating unit, for instruments determining the impurity content of liquids by measuring their electrical conductivity, comprises a resistance having a negative temp. coeff. which is shunted across the terminals of the instrument.  
J. M. JACOBS

**424. Application of the rotated dropping-mercury electrode to the analysis of mixtures of electroactive substances.** I. M. Kolthoff, Y. Okinaka and T. Fujinaga (Sch. of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1958, 18 (4), 295-309 (in English).—Poly(acrylamide) is recommended as a maximum suppressor for use with both the rotating dropping-mercury electrode (RDME) and the conventional dropping-mercury electrode (DME). It remains adsorbed on the mercury surface over the entire potential range which can be covered, and does not combine with any substance so far tested. Results are given which show that the reproducibility of residual and limiting currents at the RDME enables a single constituent to be determined at concn. as low as  $1$  to  $2 \times 10^{-8}\ M$ , with an accuracy of  $\pm 2\%$ . The variation of limiting current with potential is much greater at the RDME than at the DME, and this effect must be allowed for when using the RDME to analyse a mixture of species. Four methods are given for correcting for the effect of a previous wave on limiting current, and are discussed with reference to the analysis of mixtures of Ti and Mn in  $0.1\ M\ \text{KCl}$ , Hg and Bi in  $0.1\ M\ \text{HNO}_3$ , Ti and iodate in  $0.1\ M\ \text{KCl}$  plus  $0.05\ M$  borax, and Hg and Ti in  $0.1\ M\ \text{HNO}_3$ . It is stated that for mixtures of several species (e.g., Cu, Cd, Ni and Zn in ammoniacal medium), the same principles apply as for a mixture of two species, and results with the RDME at concn. of  $2 \times 10^{-8}\ M$  were of the same degree of accuracy as for concn. 20 times as great at the DME.  
R. E. ESSERY

**425. Use of the wide-bore dropping-mercury electrode for long-period recording of concentration of dissolved oxygen.** R. Briggs, G. V. Dyke and G. Knowles (Water Pollution Res. Lab., Stevenage, Herts., England). *Analyst*, 1958, 83, 304-311.—The apparatus described includes a new type of dropping-mercury electrode comprising a capillary tube

of 0.8 mm diameter, sloping upwards and supplied with mercury at a constant head through a capillary of bore 0.2 mm. This wide-bore electrode enables a polarographic current of  $\approx 40 \mu\text{A}$  to be produced by the reduction of dissolved oxygen, and the reference electrode (a rod of pure zinc in a buffer soln. of pH 5.5) carries this current without significant polarisation. Temp. compensation, when required, is effected by means of thermistors. One form of the apparatus records dissolved oxygen directly as p.p.m. The range is 0 to 15 p.p.m. by wt. and the mean error in two field trials was 0.00 p.p.m., with a standard deviation about this mean of 0.06 p.p.m. The method can be used either with water flowing past the electrode or with stationary samples of  $< 1 \text{ ml}$ .

A. O. JONES

**426. Evaluation of superimposed polarograms based on the measurement of current intensities below the limiting current.** G. Josepovits (Res. Inst. for Plant Protection, Budapest). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (1-2), 211-223 (in German).—Analysis of mixtures by a method that has a mean error of  $< 7\%$  is discussed. The difference between the current intensities measured at two potential values arbitrarily chosen, below the limiting current, on the relevant polarographic wave is shown to be proportional to concn. Improvement of reproducibility of potential values is achieved by using two pairs of electrodes with two galvanometers, simultaneously polarographing test and reference solutions, and interchanging electrodes to establish the mean.

E. G. CUMMINS

**427. New electrode vessel for the electrometric semi-micro determination of the oxidation - reduction**

**potential and pH of biological fluids.** O. N. Karandeeva. *Lab. Delo*, 1958, **4** (1), 50-51.—The vessel consists of two glass reservoirs (0.3 to 0.5 ml) connected by a capillary tube, the lower reservoir containing a smooth platinum electrode. The test soln. is sucked in by means of a tube attached to the upper reservoir and that part of the liquid that has been in contact with air is carried into this vessel. This eliminates effects due to atmospheric oxidation.

E. HAYES

**428. Coulometric - potentiostatic analysis in milligram range.** H. Lüdering (Max Planck Inst. Eisenforsch., Düsseldorf). *Arch. Eisenhüttenw.*, 1958, **29** (3), 173-178.—Redox reactions such as  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ ,  $(\text{HCrO}_4)^- \rightarrow \text{Cr}^{3+}$ , and  $(\text{MnO}_4)^- \rightarrow \text{Mn}^{2+}$  are measured on quantities  $> 10 \text{ mg}$  by applying a constant p.d. to two electrodes separated by a diaphragm having aq. acid on one side and a soln. of the ion involved on the other side (cf. MacNevin and Baker, *Brit. Abstr. C*, 1952, 483). The current, which falls exponentially as the reaction approaches completion, is recorded. A potentiostat, an electrolyte vessel from which air can be excluded by  $\text{CO}_2$ , and a non-chemical coulometer which amplifies and integrates the current, are described. Accuracy is checked with an electrolyte containing 10 mg of  $\text{Cu}^{2+}$ ; the recovery was  $9.99 \pm 0.03 \text{ mg}$ . Traces of Fe in tin can be determined, and the results agree satisfactorily with colorimetric data (cf. Ploum, *Anal. Abstr.*, 1959, **6**, 172). If both Fe and Cr are present, as in ferrochrome or carbides isolated from chrome steel, both are reduced at 500 mV, and Fe is then re-oxidised at 1000 mV, which is too low to re-oxidise the Cr. Results are generally within  $\pm 1\%$  of those by other methods. As little as 0.2 mg of Mn can be determined.

A. R. PEARSON

## ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current . . .	a.c.	milli-equivalent . . .	milli-equiv.
ampere . . .	amp.	milligram . . .	mg
Ångström unit . . .	Å	millilitre . . .	ml
anhydrous . . .	anhyd.	millimetre . . .	mm
approximate, -ly . . .	approx.	millimicrogram . . .	mμg
aqueous . . .	aq.	millimolar . . .	mM
atmospher-e, -ic . . .	atm.	millivolt . . .	mV
boiling-point . . .	b.p.	minute (time) . . .	min.
British thermal unit . . .	B.Th.U.	molar (concentration) . . .	M
calorie (large) . . .	kg-cal.	molecul-e, -ar . . .	mol.
calorie (small) . . .	g-cal.	normal (concentration) . . .	N
centimetre . . .	cm	optical rotation . . .	α <sub>D</sub>
coefficient . . .	coeff.	ounce . . .	oz
concentrated . . .	conc.	parts per million . . .	p.p.m.
concentration . . .	concn.	per cent. . .	%
constant . . .	const.	per cent. (vol. in vol.) . . .	% (v/v)
corrected . . .	(corr.)	per cent. (wt. in vol.) . . .	% (w/v)
crystalline . . .	}cryst.	per cent. (wt. in wt.) . . .	% (w/w)
crystallised . . .		potential difference . . .	p.d.
cubic . . .	cu.	precipitate (as a noun) . . .	ppt.
current density . . .	c.d.	precipitated . . .	pptd.
cycles per second . . .	c/s	precipitating . . .	pptg.
density . . .	ρ	precipitation . . .	pptn.
density, relative . . .	d or wt. per ml	preparation . . .	prep
dilute . . .	dil.	qualitative, -ly . . .	qual.
direct current . . .	d.c.	quantitative, -ly . . .	quant.
distilled . . .	dist.	recrystallised . . .	recryst.
ethylenediaminetetra-acetic acid . . .	EDTA	refractive index . . .	n <sub>D</sub>
electromotive force . . .	e.m.f.	relative band speed . . .	R <sub>F</sub>
equivalent . . .	equiv.	relative humidity . . .	r.h.
gram . . .	g	revolutions per minute . . .	r.p.m.
gram-molecule . . .	mole	saponification value . . .	sap. val.
half-wave potential . . .	E <sub>½</sub>	saturated calomel electrode . . .	S.C.E.
hour . . .	hr.	second (time) . . .	sec.
hydrogen ion exponent . . .	pH	soluble . . .	sol.
infra-red . . .	i.r.	solution . . .	soln.
insoluble . . .	insol.	specific gravity . . .	sp. gr.
international unit . . .	i.u.	specific rotation . . .	[α] <sub>D</sub>
kilogram . . .	kg	square centimetre . . .	sq. cm
kilovolt . . .	kV	standard temp. and pressure . . .	s.t.p.
kilowatt . . .	kW	temperature . . .	temp.
liquid . . .	liq.	ultra-violet . . .	u.v.
maxim-um, -a . . .	max.	vapour density . . .	v.d.
melting-point . . .	m.p.	vapour pressure . . .	v.p.
microgram . . .	μg (not γ)	volt . . .	V
microlitre . . .	μl	volume . . .	vol.
micromole . . .	μmole	watt . . .	W
micron . . .	μ	wavelength . . .	λ
milliampere . . .	mA	weight . . .	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than . . .	>	less than . . .	<
not greater than . . .	≥	not less than . . .	≤
is proportional to . . .	∝	of the order of, approximately . . .	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe<sup>II</sup>, Mo<sup>V</sup>. Substances in the ionic state are represented by Na<sup>+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, etc., for cations and by Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, etc., for anions.

## ANALYTICAL ABSTRACTS

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## CONTENTS

	Abstract
<b>General Analytical Chemistry</b>	
Reviews; reagents; methods of general application .. .. .	1
<b>Inorganic Analysis</b>	
General methods; elements (in order of the Periodic Table); minerals; industrial products .. .. .	17
<b>Organic Analysis</b>	
Elements and radicals; organic compounds; industrial products .. .. .	195
<b>Biochemistry</b>	
BIOLOGICAL FLUIDS; ANIMAL AND VEGETABLE TISSUES .. .. .	264
PHARMACEUTICAL ANALYSIS .. .. .	324
<b>FOOD</b>	
Food additives; beverages; edible oils and fats; vitamins .. .. .	341
<b>SANITATION</b>	
Air; water; sewage; industrial wastes .. .. .	364
<b>AGRICULTURAL ANALYSIS</b>	
Soil; fertilisers; herbicides; pesticides; animal feeding-stuffs .. .. .	378
<b>General Technique and Apparatus</b>	
GENERAL .. .. .	393
CHROMATOGRAPHY; ION EXCHANGE; ELECTROPHORESIS .. .. .	400
OPTICAL .. .. .	409
THERMAL .. .. .	418
ELECTRICAL .. .. .	422

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